SANDIA NATIONAL LABORATORIES

CHEMICAL & DISPOSAL ROOM PROCESSES DEPARTMENT 6748

WASTE ISOLATION PILOT PLANT PROJECT

TOP-553

PROCEDURE FOR BULK CHEMICAL ANALYSIS OF CULEBRA DOLOMITE FRACTURE COATINGS AND MATRIX MATERIAL

Revision 0

Effective Date: 3-14-96

	Print	Signature	Date
Author:	Charles R. Bryan	Charles R. Bryan	3/14/96
Technical Reviewer:	John W. Kelly	John R Kelly	3/14/96
PI Approval:	Larry H. Brush	L. H. Brush	3/14/96
QA Approval:	Steven P. Miller	Steven P. Miller	3/14/96
Records Center Approval:	Peggy Warner	Peggy J Warner	3/14/96

CONTENTS

1.0 REVISION HISTORY

None. This is an entirely new document.

2.0 PURPOSE

The purpose of this Sandia National Laboratories Waste Isolation Pilot Plant (WIPP) Technical Operating Procedure (TOP) is to describe the equipment and procedures to be used in the Geochemistry Laboratory of the Department of Earth and Planetary Sciences at the University of New Mexico for bulk chemical analysis of fracture coatings collected from WIPP core and hand samples of the Culebra dolomite. This work is being carried out to support evaluation of radionuclide retardation models for the Culebra Dolomite; justification for the study is described in *Test Plan for Evaluation of Dissolved Actinide Retardation at the WIPP* (Papenguth and Behl, 1996).

3.0 SCOPE

This procedure concentrates on sample handling and analysis requirements that are specific to analysis of SNL WIPP-related samples. Specific step-by-step analytical procedures are listed in Appendix C: "SNL NWRT Technical Procedure 61: Procedures for Laboratory Sample Bulk Chemical Determination." **As described in the attached memo (Appendix A), only the technical aspects of the YMP procedure apply to this WIPP TOP. Any references to YMP QA procedures are irrelevant to the WIPP Project, and do not apply to this work.**

This procedure applies to work being done by SNL personnel and contractors under work agreement WBS 1.1.10.3.1., and described in Analysis Plan AP-002, *"Mineralogical and Chemical Analysis of Fracture, Matrix, and Vug Lining Materials in Selected Culebra Dolomite Samples Collected Prior to 1991."* (Revision 0, effective date 3/11/96). It is applicable only to chemical determinations done at the Geochemistry Laboratory of the UNM Department of Earth and Planetary Sciences.

4.0 SAFETY

Chemical analyses involve the use of concentrated acids and numerous other hazardous chemicals which require special handling and precautions. All personnel who work in the Geochemistry Laboratory are specifically trained by the staff chemist in the safety procedures to be followed. General and specific precautions are summarized in Appendix C.

5.0 RESPONSIBILITIES

All SNL personnel, contractors, and other personnel working on this project have the responsibility to:

- read, understand and follow this TOP;
- obey all QA and ES&H guidelines described in this and other applicable procedures.
- obtain adequate training before engaging in the activities described herein.

The Principal Investigator (PI), or designee, whose activities warrant the use of this procedure, is responsible for implementing the requirements of this procedure.

The Project Scientist (PS), or designee, is responsible for performing the calibrations and measurements following the requirements of this procedure, documenting calibrations, and assuring that the latest revision of this document is followed.

The Quality Assurance Manager (QA Manager) is responsible for monitoring the work to assure proper implementation of the procedure and for assuring its continued effectiveness.

6.0 CONTROLS

Controls are established by written procedures or instructions prepared in accordance with QAP 5-3, PREPARING, REVIEWING, AND APPROVING TECHNICAL OPERATING PROCEDURES (Revision 1, effective date: 7/31/95) of the Sandia National Laboratories WIPP Quality Assurance Program. Procedures are issued in accordance with QAP 6-1, DOCUMENT CONTROL SYSTEM (Revision 1, effective date: 7/31/95) of the Sandia National Laboratories WIPP Quality Assurance Program.

6.1 STANDARDS

NBS-certified standards will be run with each group of samples (up to 10 samples maximum). Acceptance criteria for chemical analyses will be based on the results of the standard analyses. The ID of the standard to be used may vary with the estimated composition of the samples to be analyzed, and is at the discretion of the analyst. The ID and composition of the NBS standard used for calibration will be recorded on the Whole-Rock Analysis Data Sheets (Appendix B).

6.2 FREQUENCY

Calibration of the analytical instruments to be used will be carried out prior to analysis of each group of samples. Re-calibration will be carried out upon failure of a performance test, or in the event of any unusual occurrence (e.g. power failure), during the course of analysis of a group of samples.

6.3 PERFORMANCE TEST CRITERIA

If the variation between the measured and accepted concentrations of any element in the calibration standard exceeds 3% (10% for elements present in amounts $\leq$1.0% and $\geq$ 0.1%, 20% if <0.1% and >0.01%), then the data for that element is judged unacceptable, and must be re-determined. An exception to these limits is SiO_2, which may have variances of up to 10% if a very small sample size is used (<100 mg). If this error criteria is used, it must be noted on the Whole-Rock Analysis Worksheet.

6.4 CORRECTIVE ACTION

In the event that of a failed performance test, the element in question will be re-determined, after re-calibration of the analytical instrument. If the data still fail the calibration test, another analytical will be used.

Failures to meet acceptance criteria and the remedial action taken shall be documented on the Whole-Rock Analysis Worksheets, and in the appropriate scientific notebook. Results of the re-analysis will be entered on a new Whole-Rock Analysis Worksheet, cross-referenced to the first.

6.5 CALIBRATION

Calibration procedures for the several different analytical instruments used in this TOP are described in Appendix C, and in the instrument user manuals, available in the UNM Geochemistry Laboratory.

7.0 PROCEDURES

Detailed descriptions of the analytical procedures to be followed and the equipment to be used are described in Appendix C. Small sample sizes may require minor deviations from these procedures; *any* deviations in the procedures described in Appendix C will be fully documented in the laboratory notebook.

8.0 QA RECORDS

8.1 FORMS

Chain-of-custody forms (SNL WIPP Form 401) will be used in this procedure.

8.2 SAMPLE CHAIN-OF-CUSTODY AND DOCUMENTATION

Sample handling and documentation procedures will conform to those described in QAP 13-2 "CHAIN-OF-CUSTODY." When samples are given to the Geochemistry Laboratory for analysis, each sample will be accompanied by a chain-of-custody form, filled out and signed by the Project Scientist or his designee. These forms will be signed and dated by the Department of Earth and Planetary Sciences Staff Chemist when received and the chain-of-custody form will be processed in accordance with QAP 13-2.

If necessary, the Staff Chemist will assign a short form name to the samples which will be used in all Geochemistry Laboratory logbooks. All logbook entries will be made in black, indelible ink, with any corrections lined through, initialed and dated. This name must be entered in the appropriate place on each chain-of-custody form to provide the means of cross-referencing internal lab numbers with the full SNL WIPP sample ID. The laboratory notebook used to log samples into the lab must contain a complete cross-reference to the full and shortened sample IDs.

The staff chemist will make one copy of each signed form and return them within 3 days to the Project Scientist, who will file them in a sample logbook. The original forms will be kept in the Geochemistry Laboratory with the samples until analysis is completed and any remaining sample material is transmitted back to the Project Scientist.

Samples transmitted to the Geochemistry laboratory will consist of small rock fragments and powder scraped or ground from fracture surfaces of hand and core samples. Samples will be transmitted in sealed sample containers labeled with indelible black ink; labels will be protected with tape. Whole rock chemical analysis is a destructive process; fractions of the sample removed are consumed in the analytical process. Each time a container is opened and some of the sample is removed for analysis, the mass of the sample removed will be noted on the chain-of-custody form along with the date and signature of the person removing the material.

After all analytical work is completed, and a summary report of results obtained by the Geochemistry Laboratory is prepared, the remaining sample material will be returned to the Project Scientist along with the signed chain-of-custody forms.

8.3 DATA DOCUMENTATION AND REPORTING

QA records, including corrections and changes thereto, generated as a result of implementing this procedure, shall be prepared and submitted to the SNL WIPP Center File (SWCF) in accordance with QAP 17-1 "WIPP QUALITY ASSURANCE RECORDS SOURCE REQUIREMENTS". The following records, if generated by use of this TOP, shall be designated as QA records:

1. Entries in the experiment notebook, including: notes on sample preparation, any deviations from the procedures described here, and the reasons for them, and any unusual occurrences noted during the course of chemical analysis.
2. Sample Whole-Rock Analysis Worksheets, which will be generated for each group of samples (up to 4 per group. This worksheet will include basic information about the samples, (Full Sample and Lab ID, SNL Principle Investigator, etc.), plus a list of all elements analyzed, the method used to obtain the analysis, date of analysis, analytical results, and notations about any unusual occurrences. For AA and XRF analysis, results obtained for the NBS or other standard used will be listed on the worksheet. The percent variation in the standard will be calculated and used as specified in the worksheet to determine acceptability of the analysis. An example worksheet is given in Appendix B.
3. A copy of all computer printouts, strip charts, standard curves (if AA analysis is used), appropriate pages in laboratory notebooks, Whole-Rock Analysis Worksheets, and any related documentation will be submitted to the Project Scientist at the conclusion of data gathering. A brief summary report, tabulating results for all samples, will be included in this material.

All written records generated during the use of this TOP will be recorded using black, indelible ink. Laboratory notebook entries will conform to the guidelines described in WIPP QAP 20-2, "PREPARING, REVIEWING, AND APPROVING SCIENTIFIC NOTEBOOKS" (Rev. 1, 7/31/95). Periodic reviews of scientific notebooks will be performed to insure that these guidelines are followed.

8.4 NONCONFORMANCE AND DEVIATION REPORTING

Nonconformance, deviation, and corrective action reporting will be in accordance with QAP 16-2, "CONDITIONS ADVERSE TO QUALITY AND CORRECTIVE ACTION."

9.0 REFERENCES

Papenguth, H., and Behl, Y, 1996. *Test Plan for Evaluation of Dissolved Actinide Retardation at the WIPP.*

Siegel, Malcolm D., 1996. *Mineralogical and Chemical Analysis of Fracture, Matrix, and Vug Lining Materials in Selected Culebra Dolomite Samples Collected Prior to 1991*, SNL Analysis Plan AP-002.

SNL NWRT Technical Procedure TP-61: PROCEDURES FOR LABORATORY BULK CHEMICAL DETERMINATION (Revision A, effective date 2/2/90).

QAP 5-3, PREPARING, REVIEWING, AND APPROVING TECHNICAL OPERATING PROCEDURES (Revision 1, effective date: 7/31/95).

QAP 6-1, DOCUMENT CONTROL SYSTEM (Revision 1, effective date: 7/31/95).

QAP 13-2, CHAIN-OF-CUSTODY (Revision 1, effective date 7/31/95).

QAP 16-2, CONDITIONS ADVERSE TO QUALITY AND CORRECTIVE ACTION (Revision 1, effective date 7/31/95).

OAP 17-1, WIPP QUALITY ASSURANCE RECORDS SOURCE REQUIREMENTS (Revision 1. effective date 7/31/95).

QAP 20-2, PREPARING, REVIEWING, AND APPROVING SCIENTIFIC NOTEBOOKS (Revision 1, effective date 7/31/95).

APPENDIX A: Authorization Memo

Sandia National Laboratories

P. O. Box 5800
Albuquerque, New Mexico 87185-1320

Managed by Sandia Corporation
a Lockheed Martin Company

WBS: 1.1.10.3.1

date: March 12, 1996

to: File

Malcolm Siegel J T Holmes

from: M. D. Siegel, 6748, J. T. Holmes, 6748

subject: Use of Yucca Mountain Project Technical Procedures as Appendix A in WIPP TOP 553.

Procedures for bulk chemical analyses of clay-sized material were developed and implemented at the Geochemistry Laboratory (Dept. of Earth and Planetary Sciences) of the University of New Mexico for the Yucca Mountain Project in 1990. The same procedures will be used in the work described by WIPP TOP-553; therefore a copy of the approved YMP procedures are included as Appendix A. As noted in TOP-553, only the technical aspects of the YMP procedures apply to the WIPP studies. All references to YMP QA procedures are considered irrelevant to the WIPP Project and do not apply to this work. It is our opinion that the additional work required to rewrite the procedures is not justified at this time and that the quality assurance control of the work or documentation will not be affected.

Enclosures:

Distribution
SWCF-A:1.1.10.3.1; clays

APPENDIX B: Whole-Rock Analysis Worksheet

Major Element Whole-Rock Analysis Worksheet

1. SNL-WIPP Information

EP ID & Revision:________________________Worksheet #____________

Analyst name:________________________Signature____________

Date:____________Analysis Location:________________________

SNL PI:________________________Division__________Phone__________

2. Sample Information:

Indicate the # of samples in this group (Maximum 4):__________

Sample #1 Full ID________________________Brief (Lab) ID:____________

Sample #2 Full ID________________________Brief (Lab) ID:____________

Sample #2 Full ID________________________Brief (Lab) ID:____________

Sample #2 Full ID________________________Brief (Lab) ID:____________

3. Calibration Check for Elements Determined by XRF or AA:

If for AA, indicate worksheet #'s for which this check is used: __________

Calibration Check Standard Used:________________________

Element: SiO_2	TiO_2	Al_2O_3	Fe_2O_3*	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total
Std. amts:										
Analyzed:										
% Variation:										

* total iron reported as Fe_2O_3.

If any of the calculated variation values exceed 3% (10 % for elements present in amounts <1% and > 0.1%, 20% if <0.1% and >0.01%), either the equipment will be re-calibrated and that element re-determined, or an alternative method used (if only very small sample sizes are available, acceptable errors for SiO_2 may be as large as 10%; this will be noted in the appropriate scientific notebook).

4. Acceptance Criteria / Re-determination Indication

XRF and AA data are judged by criteria in Section 3 (above). If data for any element determined is judged unacceptable, ERR will be marked on this data sheet (Sec. 5) and a new data sheet prepared for re-determined elements.

Check here if this sheet is for re-determined data:__________

5. Whole-Rock Analysis Results

Sample ID:								
Element:	Amt.	Test	Amt.	Test	Amt.	Test	Amt.	Test
SiO_2								
TiO_2								
Al_2O_3								
Fe_2O_3								
FeO								
MnO								
MgO								
CaO								
Na_2O								
K2O								
P_2O_5								
H_2O^+								
H_2O^-								
Total:								
Fe2O3*								
LOA								
FeO (after LOA)								

Notes: All reported amounts (Amt.) are weight percentages. ERR adjacent to number in column indicates results out of specification, requiring re-determination (results recorded on another sheet); BD. indicates amount reported is below detection limit for analytical technique used.

Test types: XRF = X-Ray Fluorescence AA = Atomic Adsorption C = Colorimetric Analysis
V = Volumetric Analysis G = Gravimetric Analysis

APPENDIX C:

SNL NWRT TP-61: PROCEDURES FOR LABORATORY SAMPLE BULK CHEMICAL DETERMINATION

SNL NWRT Department Technical Procedure
Procedures for Laboratory Sample Bulk Chemical Determination

Page	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	18	19	20	21	22	23
Rev.	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A

Page	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43
Rev.	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A

Page	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62
Rev.	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A	A

Page	63	64	65	66	67	68	69	70	71	72
Rev.	A	A	A	A	A	A	A	A	A	A

Co-Author: ______________________ 1/5/90
James R. Connolly — Date
Project Research Scientist
UNM, Institute of Meteoritics

Co-Author: ______________________ 1/5/90
John W. Husler, Staff Chemist — Date
UNM, Department of Geology

Approved: ______________________ 1/22/90
Klaus Keil, Director — Date
UNM, Institute of Meteoritics

Approved: ______________________ 1/8/90
Francis B. Nimick, 6313 — Date
SNL Principal Investigator

Approved: ______________________ 1/11/90
F. J. Schelling, 6316 — Date
Independent Technical Review

Approved: ______________________ 1-12-90
R.R. Richards, 6310 for — Date
Quality Assurance

Approved: ______________________ 1/17/90
Thomas E. Blejwas, 6313 — Date
Division Supervisor

Effective Date: 2/2/90

1. PURPOSE

This technical procedure (TP) along with associated "in-house" documents included here as appendices describe the equipment and procedures used in the Geochemistry Laboratory in the Department of Geology and Institute of Meteoritics (IM) at the University of New Mexico (UNM) to perform whole-rock chemical analyses on rock or mineral samples provided by Sandia National Laboratories (SNL) as part of the Yucca Mountain Project (YMP). (Note: This project is referred to as the Nevada Nuclear Waste Storage Investigations or NNWSI Project in documents written prior to last quarter of 1988.) The "in-house" documents are concerned with the step-by-step procedures followed in various analytical and sample preparation techniques used in the Geochemistry Laboratory, and this TP concentrates on sample handling and analysis requirements which are specific to analysis of SNL YMP-related samples.

For most SNL YMP work, a whole-rock analysis will consist of weight percentages of major element oxides, including SiO_2, TiO_2, Al_2O_3, FeO, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, $H_2O(-)$, and $H_2O(+)$. This TP is explicitly concerned with analysis for these elements. Should analysis for other elements be required for a particular task, the technique(s) appropriate to the analysis for those elements will be specified in the Experiment Procedures (EP) governing the work, and/or incorporated in subsequent revisions of this TP.

Several analytical methods can be used to determine the composition of whole-rock samples. Most elements may be determined by X-ray fluorecence spectrometry or by a combination of atomic absorption spectrophotometry combined with gravimetric determination of silica (SiO_2) and spectrophotometric determination of phosphorous (P_2O_5). Slightly greater accuracy and precision for most elements of interest may be attained using atomic absorption, but the procedures are considerably more time consuming and complex. The method, or mix of methods, to be used will be specified in the EP governing the work. FeO is determined volumetrically, and H_2O is determined gravimetrically by measurement of the sample weight change upon heating. Details of the procedures are discussed in subsequent sections and in appendices.

2. SCOPE

This TP applies to any rock or mineral sample or standard reference material (SRM) provided by SNL for study in conjunction with an SNL YMP EP which governs the work.

Whole-rock analysis procedures described in this document are used to provide data on the chemical composition of the material to be analyzed. Data are reported as weight percents (wt %) of constituents, generally expressed as metal oxides (SiO_2, Na_2O, FeO, etc.). Analytical techniques used to obtain these data may vary somewhat depending on the samples and the elements for which analyses are to be done. Analytical objectives and requirements are detailed in an EP provided to UNM by the SNL Principal Investigator (PI).

3. DEFINITIONS

Atomic absorption spectrophotometry (AA), X-Ray fluorescence spectrometry (XRF), gravimetric analysis, and other techniques of chemical analysis discussed here are described and discussed in a number of standard reference texts including Furman (1962), Kolthoff and Sandell (1952), Vogel (1961), and Willard et al. (1965). Brief descriptions of the techniques may be found in Parker (1982).

4. EQUIPMENT AND SOFTWARE RESOURCES

4.1. Equipment Used

4.1.1. General Laboratory Equipment

-> Class A laboratory glassware including:
50 mL burets for titration (with 0.1 mL divisions)
100 mL volumetric flasks (for AA solutions)
10 mL pipets (for AA solutions)
(plus other items as needed)

-> Automatic dispenser, Repipet (R) or equivalent (for Cs-HCl reagent for AA)

-> Corning (R) laboratory hot plates (for warming and heating of various solutions, reagents, and materials).

-> Various sizes of platinum (Pt), and platinum-gold (Pt-Au) crucibles (for sample fusions for XRF and other procedures).

-> Thelco drying oven (for heating to 110±10 °C)

-> Lindberg Model 51848 laboratory box furnaces (for heating to 1000±70 °C)

-> Ohaus Model G 110 balance (Serial #5050) (Measurement range 0-110 g, readable to ±0.0001 g, accurate to ±0.0002 g, calibrated annually using weights tracable to NBS standard weights.)

-> Mettler H16 laboratory balance (Serial #124904). (Measurement range 0-80 g, readable to ±0.00005 g, accurate to ±0.0001 g, calibrated annually using weights tracable to NBS standard weights)

-> Miscellaneous laboratory equipment (beakers, stirring rods, polyethelene bottles, and other items as needed)

4.1.2. XRF Equipment

-> Rigaku 3064M X-ray fluorescence spectrometer (Serial #DR12035) equipped with a Machlett Rh-target, end-window X-ray tube (Model Number OEG-75G3).

-> Hokushin Model RR130-2-H114-030-090 strip chart recorder (Serial #5B7086A0110K).

-> Digital Equipment Corporation (DEC) Micro PDP-11/73 with DEC RX02 8 1/2" dual floppy disk drive and a 30 megabyte hard disk drive housed in a DEC 11V03-L cabinet and equipment rack.

-> DEC Decwriter III Terminal.

4.1.3. AA Equipment

-> Perkin Elmer Model 303 atomic absorption spectrophotometer (Serial #34872)

-> Perkin Elmer Model 165-0045 strip chart recorder (Mfgr. #K216649).

-> Various cathode tubes for the elements to be analyzed. (See Appendix C for details.)

4.1.4. Spectrophotometric Equipment

-> Bausch & Lomb Spectronic 88 spectrophotometer (Catalog #33.30.42, Serial #020938J

-> 1-cm colorimeter cells (for holding solutions during analysis)

4.2 SOFTWARE USED

4.2.1 X-Ray Fluorescence Software

-> Digital Equipment Corporation's (DEC) RT-11 operating system (Version 5) is used on the DEC PDP-11/73.

-> Rigaku/USA, Inc., 3064 Dataflex (Ver. 3-1) is used for collection XRF data. This software package is used for equipment control, data gathering, data reduction, and output for all major element XRF analysis.

Requirements for verification of software used in data collection are detailed in the EP governing the work.

5. PROCEDURES

The project logbook maintained by the Project Research Scientist (including Whole-Rock Analysis Worksheets--Appendix A), the sample Chain-of-Custody forms, and any entries made in Geochemistry Laboratory notebooks regarding analysis of YMP samples must be filled out in black indelible ink. Any corrections made to entries in the log books must be made by lining-through the incorrect entry, initialing and dating in such a manner that the original entry is still readable.

The procedures used to obtain a whole-rock chemical analysis begin with preparation of a finely-ground powder of the sample. If XRF will be used, a fused disk is prepared from a portion of the powder. A check of the accuracy of the XRF technique is made with each group of samples analyzed by simultaneously analyzing a known NBS rock standard for each element simultaneously with the samples. Water content is obtained by gravimetric determination of weight lost on ignition, coupled with volumetric determination of ferrous iron (FeO) in both the ignited and unignited sample. Details of the procedures are contained in Appendices B, D, E, F, and G, and in later sections of this TP.

If AA will be used, solutions of samples and standard are prepared and analyzed simultaneously. For every batch of 10 (or fewer) samples analyzed, an NBS rock standard will be analyzed to check the accuracy of the technique. SiO_2 is determined gravimetrically, P_2O_5 is determined by spectrophotometrically, and water content is obtained by gravimetric determination of weight lost on ignition, coupled with volumetric determination of ferrous iron (FeO) in both the ignited and unignited sample. Details of the procedures are contained in Appendices C, E, F, G and H, and in later sections of this TP.

Various types of Class A volumetric glassware (ASTM Standard E 694) are used in several of these procedures. Table 1 summarizes the measurement tolerances specified by ASTM for the glassware used.

Table 1. ASTM Standards for Class A Laboratory Glassware

Item-Capacity	Divisions	Tolerance (±)	ASTM Ref.
Buret-50mL	0.1mL	0.05mL	E 287
Volumetric Flask-100mL	NA	0.08mL	E 288
Pipet-10mL	NA	0.02mL	E 969

5.1. Preparation of Samples for Analysis

5.1.1. Sample Crushing and Powdering

Samples to be analyzed must be powdered to a fine uniform grain size and randomly split to assure high quality analyses. The procedures used are specified in TP-59 (Procedures for Laboratory Sample Petrology Determination).

5.1.2. Preparation of Fused Disks for XRF Analysis

To analyze for major elements, fused disks are prepared using procedures outlined in Appendix B. As part of the procedure, all fused disks are labeled with the Lab ID number discussed in section 6.1.

5.1.3. Preparation of Solutions for Atomic Absorption (AA) Analysis.

Procedures followed in preparation of standard and sample solutions for use in AA analysis are detailed in Appendix C. To obtain the most accurate results, the Mettler balance should be used. Solutions need to be prepared only if AA is to be used to obtain analytical data, either as required in an EP governing the work or as a check of results obtained by XRF.

5.2. X-Ray Fluorescence (XRF) Analysis for Major Elements

Procedures for obtaining major element analytical data using the Rigaku X-Ray Fluorescence Spectrometer are detailed in Appendix D. The sections which follow are specific to the calibration check required when analyzing YMP Samples with XRF.

5.2.1. For each group of up to four YMP samples, a standard of composition similar to the samples being analyzed (either NBS SRM-278 [Obsidian] or NBS SRM-688 [Basalt] or some other standard as specified in the governing EP) is run with the group as a check on the accuracy of the analysis. The XRF has positions for 6 samples; a drift correcting standard (usually USGS Basalt standard BCR-1) is always in position 1. Any one of the other 5 positions will be an NBS rock standard and the remaining 4 positions will be YMP samples.

5.2.2. After data have been collected, the analysis of the NBS standard will be compared with the accepted analysis for the material given by NBS. Analytical data must agree within the following limits: ±3.0% of the amount present for amounts greater than 1 wt.% of the total, ±10.0% for amounts ≤1.0 wt.% and ≥0.1 wt.%, ±20% for amounts <0.1 wt.% and >0.01 wt.%. Amounts ≤0.01 wt.% are considered below the detection limit for XRF. This comparison is made on the Major Element Whole-Rock Analysis Worksheet (Appendix A). If these data do not agree, then data for elements not in agreement will not be used. The code ERR will be entered next to the amounts determined for the samples on the Major Element Whole-rock Analysis Worksheet, and noted as an Unusual Occurrence (Appendix A, Sections 5 & 6). The element(s) are redetermined with data recorded on another worksheet including a notation in Section 4 of the worksheet. Redetermination may be by XRF (after recalibration), or by another technique (AA, gravimetric, etc.) appropriate for that element.

5.3. Gravimetric Determination of Water Loss on Ignition (LOI)

Water content of a whole-rock sample is determined by measurement of the weight lost during heating. First the powdered sample is weighed, placed in a pre-heated low temperature drying oven (at 110±10 °C) for approximately one hour, cooled in a desiccator for one hour, and reweighed; the percentage weight loss is then calculated (as a percentage of the original weight) to yield the amount of $H_2O(-)$. This same weighed sample is then ignited in a furnace pre-heated to 1000±70 °C for about 1 hour, cooled for one hour in a desiccator and reweighed. Special care is taken to minimize the time between removal of a sample from the desiccator and actual time of weighing to minimize absorbtion of water by the sample. After a correction for weight gained on ignition by oxidation of FeO to Fe_2O_3 (see Section 5.4), the LOI is reported as $H_2O(+)$ in wt. %. Details of these procedures (including equations used in calculations) are discussed in Appendix E. Other volatiles, including carbonate and organic matter will be included in the estimation of $H_2O(+)$.

For all SNL-YMP samples analyzed, all weighings are done using one of the two balances mentioned in section 4.1.1. All weighings for each group of samples are done on the same balance. For the highest precision work, the Mettler balance will be used.

5.4. Determination of Ferrous Iron (FeO)

In both XRF and AA, total iron content in a sample total is reported as Fe_2O_3, as if it were all in the ferric state. A volumetric titration procedure is used on a portion of the powdered sample to determine how much of that total iron is in the ferrous state (as FeO). A similar determination is made on the ignited sample (See Section 5.3) to correct LOI amounts for weight gained due to oxidation of ferrous iron. Details of the procedures (including calculations) are discussed in Appendix F.

For all SNL-YMP samples analyzed, only Class A laboratory burets will be used for the titrations (Section 4.1.1.). Prior to analyzing samples under a SNL YMP EP, 3 to 5 splits of a known standard will be analyzed to determine precision and accuracy for the technique. The specific standard used will be specified in the governing EP.

5.5. Atomic Absorption (AA) Analysis for Major Elements

Atomic Absorption Spectrophotometry (AA) may be used for determination of all major elements except SiO_2, FeO and P_2O_5. These elements are not amenable to accurate determination by AA, and are determined by techniques described in other sections of this TP. AA may be used as the primary analytical technique, as a backup for XRF, or as a check on XRF for a portion of the samples to be analyzed. This will be specified in the EP governing the work and/or in consultation with the SNL PI.

Procedures for determining major elements using AA are detailed in Appendix C. The sections which follow include only procedures specific to analysis of SNL YMP samples not addressed in that document.

5.5.1. Standard solutions are prepared as described in Appendix C (Husler 1988a). In-house rock standards (usually UNM-B1 Basalt), which have been analyzed against an internationally recognized standard rock (usually an NBS rock standard named in the governing EP) or NBS standards may be used. Since some of the standard is consumed in the analysis, use of in-house standards preserves the recognized standard material for future use. The method of selecting the standard to be used is specified in the EP governing the work. Strip charts and calibration curves used to analyze the NBS and in-house standards are retained and copies made for the project files as required in the governing EP.

5.5.2. For each group of sample (up to a maximum of 10) and standard solutions prepared, one set of solutions will be prepared from a known rock standard (either NBS SRM-278 [Obsidian] or NBS SRM-688 [Basalt] or some other standard specified in the governing EP). The standard will then be determined in the normal manner, and used to verify the accuracy of the procedure.

5.5.3. After the data have been collected and amounts determined, the analysis of the known standard will be compared with the accepted analysis for the material. Analytical data must agree within the following limits: ±3.0% of the amount present for amounts greater than 1 wt.% of the total, ±10.0% for amounts ≤1.0 wt.% and ≥0.1 wt.%, ±20% for amounts <0.1 wt.% and >0.01 wt.%. Amounts ≤0.01 wt.% are considered below the detection limit. This comparison is made on the Major Element Whole-Rock Analysis Worksheet (Appendix A). If these data are outside these limits, then data for elements not in agreement will not be used. The code ERR will be entered next to the amounts determined for the samples on the Major Element Whole-rock Analysis Worksheet, and noted as an Unusual Occurrence (Appendix A, Sections 5 & 6). The element(s) are redetermined with data recorded on another worksheet, including a notation in Section 4 of the worksheet. Redetermination may be by AA (using another set of prepared solutions), or by another technique (XRF or other method) appropriate for that element.

5.5.4. Two photocopies of any notes recorded in geochemistry laboratory notebooks regarding sample preparation will be made and given to the Project Research Scientist (PRS) at the completion of data gathering, or as specified in the governing EP.

5.5.5. AA data are recorded on strip charts in which various concentration standard solutions (and the blank) are run with the samples. These strip charts will be marked (in black indelible ink) with the name of the element being analyzed, an appropriate reference number for the sample (usually the SNL YMP sample ID or a shortened LAB ID; See Section 6.1), the name of the analyst, and the date the data were collected. If specifically requested in the governing EP, a photocopy (or copies) of all strip charts will be made available for transmittal to the PRS as detailed in Section 6.2.

5.5.6. As detailed in Appendix C, determination of element concentration is acomplished by construction of standard curves of percent absorption vs. concentration in the standard rock (in wt. %) for each element using standard solutions of various concentrations. Percent absorption of sample (unknown) solutions are plotted on the standard curves to yield wt % in the unknown rock. For all SNL-YMP work, these standard curves will be constructed in black, indelible ink and transmitted to the PRS as detailed in Section 6.2.

5.5.7. The flame changes color notably during analyses. If flame color does not return to approximately what it was after no longer aspirating a sample, or the burner is making unusual noises, IMMEDIATELY close the C_2H_2 safety valve. Data collected between standard runs prior to this point may be used. For data collected after the last run of standards, a notation will be made on the strip chart and the data not used. Data will be re-collected after checking the AA and resetting the flame and strip chart recorder as detailed in Appendix C.

5.6. Gravimetric Determination of Silica (SiO_2)

If AA is used to determine other elements, SiO_2 will be determined gravimetrically. XRF, when used to determine other elements, will be used to determine SiO_2 also; if XRF results are questionable for SiO_2, a gravimetric determination should be performed as an alternative.

To determine SiO_2 gravimetrically, the sample is fused with sodium carbonate, leached with HCl, dehydrated, and the silica filtered, ignited, and weighed. Detailed procedures are described in Appendix G. The sections which follow include only procedures specific to analysis of SNL YMP samples not addressed in that document.

5.6.1. For all SNL YMP samples, the "Long Method" (Appendix G; Husler, 1988d) utilizing a double precipitation and volatilization with hydrofluoric acid will be used.

5.6.2. In this procedure, all data on preparation of reagents and weighings are recorded in a Geochemistry Laboratory notebook. Two photocopies of the appropriate pages will be forwarded to the PRS at the completion of data gathering.

5.6.3. For all SNL-YMP samples analyzed, all weighing of samples will be done using one of the two balances in section 4.1.1. All weighings for each group of samples will be done on the same balance. The Mettler balance should be used due to its greater accuracy.

5.7. Colorimetric Determination of Phosphorus (P_2O_5)

If AA is used to determine other elements, P_2O_5 will be determined colorimetrically. XRF, when used to determine other elements, will be used to determine P_2O_5 also; if XRF results are questionable for P_2O_5, a colorimetric determination should be performed as an alternative.

The Bausch & Lomb Spectronic 88 Spectrophotometer is used for the phosphorus (as P_2O_5) determination using a modification of the Molybdenum Blue method as described in Appendix H. The following sections include only procedures specific to analysis of YMP samples not addressed in that document.

5.7.1. As with AA analysis (Sect. 5.5.1) in-house standard solutions traceable to an internationally recognized standard rock will be used.

5.7.2. Since amounts of P_2O_5 are read directly from a meter on the spectrophotometer, the only records for these analyses are entries in a geochemistry laboratory notebook. Two photocopies of the notebook pages will be made and given to the PRS.

6. SAMPLE HANDLING AND DOCUMENTATION

6.1 Sample Custody and Logging

When samples are given to the Geochemistry Laboratory for analysis, each sample will be accompanied by a chain-of-custody form, filled out, dated and signed by the PRS (or equivalent as specified in the governing EP). These forms will be signed and dated by the Staff Chemist when received.

If not already done by the PRS, the Staff Chemist will assign the short form name to the samples which will be used in all Geochemistry Laboratory logbooks. All logbook entries must be made in black, indelible ink (with any corrections lined-through, initialed and dated). This name must be entered in the appropriate place on each chain of custody form to provide the means of cross referencing internal lab numbers with the full SNL YMP sample ID.

The Lab IDs should include some short version of the number of the Experiment Procedure assigned to the work, plus a unique number for that sample. As an example, if sample G-1 1721.2A is the third sample in a list of samples being analyzed under EP-0027, it could be assigned the shortened ID: EP27-WR3 as a workable lab number. The WR prefix indicates whole rock analysis. The laboratory logbook used to log samples into the lab must contain a complete cross reference to the full and shortened sample IDs.

The Staff Chemist will then make two (2) copies of each signed form and return them within three days to the PRS who will file one copy and forward the other to SNL PI. The original forms will be kept in the Geochemistry Laboratory with the samples, until analysis is completed and remaining sample powder (see below) is transmitted back to the PRS following appropriate custody procedures referenced in the governing EP.

In general, samples transmitted to the Geochemistry Laboratory will be in the form of powders prepared according to procedures detailed in TP-59. The powders will be transmitted in sealed sample containers which will be marked and handled as specified in the governing EP. Whole-rock chemical analysis is essentially a destructive process, and fractions of sample removed are consumed in the analytical process. Each time the sample container is opened and some of the sample removed for analysis, the mass of sample removed (in grams) will be noted on the chain of custody form along with the date and signature of the person removing some of the sample. After sample material is removed, a new seal will be affixed to the sample container and a notation will be made on the chain of custody form.

After all analytical work is completed, and a summary report of results obtained by the Geochemistry Laboratory is prepared, the remaining sample material will be returned to the PRS with appropriate signatures on the chain-of-custody forms.

6.2 Documentation Requirements

For each group of samples (up to 4 per group) analyzed, a Sample Whole-Rock Analysis Worksheet (Appendix A) will be prepared. This worksheet will include basic information about the samples (Full Sample and Lab ID, governing EP, SNL PI, etc.), plus a list of all elements analyzed, the method used to obtain the analysis, the date of the analysis, analytical results, and notations about any unusual occurrences. Although procedures for dealing with nonconformances will be specified in the governing EP, any unusual occurrences or nonconformances should be reported as soon as possible to the PRS who will consult with the SNL PI. For AA and XRF analysis, results obtained for the NBS or other standard used (SRM-278, SRM-688 or as specified in the governing EP) will be listed on the worksheet. The percent variation from reported amounts in the standard will be calculated and used as specified in the worksheet (Appendix A, Section 3) to determine acceptability of the analysis.

Two (2) copies of all computer printouts, calculations used in arriving at analytical results, strip-charts (if specifically requested in the governing EP), standard curves (if AA analysis is used), appropriate pages in laboratory notebooks, and any related documentation will be made by the Staff Chemist or a designated assistant within five (5) days of the time of data gathering and transmitted to the PRS at the conclusion of the data gathering. A brief summary report to the PRS tabulating analytical results for all samples will be included with this material. One copy of all material will be included in the project files in the IM and another copy transmitted to SNL for inclusion in the appropriate Data Records Management System (DRMS) file. All of these documents are the quality assurance (QA) records for the YMP. The summary report and individual Whole-rock Analysis Worksheets (Appendix A) will be incorporated in the Experiment Log Book kept for the governing EP.

6.3 Nonconformance and Deviation Reporting

Procedures for handling of any deviations or nonconformances which occur during the performance of the procedures will be specified in the EP governing the work. Except as modified in the governing EP, nonconformance reporting will be in accordance with QAP 15-1, deviation reporting will be detailed in accordance with QAP 16-2 and corrective action reporting will be initiated in accordance with QAP 16-1.

7. SAFETY

Chemical analyses involve the use of concentrated acids (hydrofluoric, hydrochloric and nitric) and numerous other chemicals which require special handling and precautions. All personnel who work in the Geochemistry Laboratory are specifically trained by the Staff Chemist in the safety procedures to be followed. General precautions are summarized below. Specific precautions are discussed in the appropriate in-house documents describing the procedures (Appendices B-H).

1. Safety glasses (or prescription glasses with safety glass lenses) and laboratory clothing (including gloves) are worn at all times when working with chemicals in the laboratory.

2. All heating of solutions containing concentrated acids or other potentially toxic solutions is done under an operating fume hood.

3. All work with concentrated hydrofluoric acid is done under an operating fume hood.

4. When crushing and powdering rock samples in an enclosed area, both safety glasses and dust masks are worn.

5. Heat resistant gloves and protective laboratory clothing are worn during heating of solutions over flame or over a hotplate, and long tongs are used to handle the platinum crucibles or other laboratory ware used in these operations.

6. Emergency shower facilities and fire extinguishing equipment are available in the laboratory.

8. REFERENCES

ASTM (American Society for Testing and Materials). The procedures listed below have been cited in this document. Because all ASTM procedures are reviewed and updated periodically, no date is assigned to these references. The most recent version prior to December, 1988 is to be assumed in all cases.

E 287 Standard Specification for Burets
E 288 Standard Specification for Volumetric Flasks
E 694 Standard Specification for Volumetric Ware
E 969 Standard Specification for Volumetric (Transfer) Pipets

Furman, N. H. (Editor), Standard Methods of Chemical Analysis, 6th Edition, D. Van Nostrand Co., Inc., Princeton, N.J., 1962.

Kolthoff, J. M., and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, 3rd Edition, The Macmillan Co., New York, 1952.

Parker, Sybil P. (Editor), and others, McGraw Hill Encyclopedia of Chemistry, McGraw Hill, Inc., New York, 1195 p., 11982.

SNL NWRT Department Operating Procedure QAP 15-1, Nonconformance Control and Reporting for Items and Activities.

SNL NWRT Department Operating Procedure QAP 16-1, Corrective Action Reporting.

SNL NWRT Department Operating Procedure QAP 16-2, Deviation Reporting.

SNL NWRT Department Technical Procedure TP-59, Procedures for Laboratory Sample Petrology Determination.

Vogel, Arthur I., A Textbook of Quantitative Inorganic Analysis, 3rd Edition, John Wiley and Sons, Inc., New York, 1961.

Willard, Hobart H., Merritt, Lynne L., and Dean, John A., Instrumental Methods of Analysis, 4th Edition, D. Van Nostrand Company, Inc., Princeton, N.J., 784 p., 1965.

Major Element Whole-Rock Analysis Worksheet

1. SNL-YM Project Information:

EP ID & Rev:______________________________ Worksheet #:______________
Analyst Name:______________________ Signature:______________________
Date:__________ Analysis Location:______________________________
SNL PI:______________________ Division:__________ Phone:__________

2. Sample Information:

Indicate # of samples analyzed in this group (Maximum 4):______

Sample #1 Full ID:______________________ Brief (Lab) ID:__________
Sample #2 Full ID:______________________ Brief (Lab) ID:__________
Sample #3 Full ID:______________________ Brief (Lab) ID:__________
Sample #4 Full ID:______________________ Brief (Lab) ID:__________

3. Calibration Check for Elements Determined by XRF or AA:

If for AA, indicate Worksheet #s for which this check is used:____________

Calibration Check Standard Used (Check One): SRM-688 (Basalt):_____ SRM-278 (Obsidian):_____
Other (fill in name here and name and amounts below):

Element:	SiO_2	TiO_2	Al_2O_3	Fe_2O_3*	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total
Std Amounts:											
SRM-688	48.4	1.17	17.36	10.35	0.167	8.4a	12.17a	2.15	0.187	0.134	100.488
SRM-278	73.05	0.245	14.15	2.04	0.052	0.23a	0.983	4.84	4.16	0.036	99.786
________											
Analyzed:											
% Variation**											

* Total Iron reported as Fe_2O_3. a Indicates values reported (but not certified) by NBS.

$$** \text{ Calculated \% Variation: } \frac{\text{(Analyzed Amount - NBS Amount)}}{\text{NBS Amount}} \times 100 \quad \text{(Amounts in Wt. \%)}$$

If any of calculated % Variation values exceed 3% (10% for elements present in amounts ≤1.0% and ≥0.10%, 20% if <0.1% and >0.01%), either the XRF or AA equipment will be recalibrated and that element redetermined, or an alternative method used.

4. Acceptance Criteria / Redetermination Indication

XRF and AA data are judged by criteria in Section 3 (above). Complete analyses with analytical totals for elements in Section 5 between 99.0% and 100.5% are judged acceptable. If data for any element determined is judged unacceptable, ERR will be marked on this data sheet (Sec. 5), and a new data sheet prepared for redetermined elements.

Check here if this data sheet is for is redetermined data: ________

5. Whole-Rock Analysis Results

Sample ID:								
	Amt.	Test	Amt.	Test	Amt.	Test	Amt.	Test
Element:								
SiO_2								
TiO_2								
Al_2O_3								
Fe_2O_3								
FeO								
MnO								
MgO								
CaO								
Na_2O								
K_2O								
P_2O_5								
H_2O^+								
H_2O^-								
Total:								
Tot. Fe (Fe_2O_3)								
LOI								
FeO (after LOI)								

Notes: All reported amounts (Amt.) are weight percentages. ERR adjacent to number in column indicates results out of specification requiring redetermination (results recorded on another sheet); BDL indicates amount reported is below detection limit for analytical technique used.

Test types:
- XRF = X-Ray Fluoresence
- AA = Atomic Absorption
- C = Colorimetric Analysis
- V = Volumetric Analysis
- G = Gravimetric Analysis

6. Unusual Occurrences

Discuss below any unusual occurrences (variation from standard techniques, analytical totals outside of accepted limits) during gathering of whole-rock data. Check here ____ if continued on another sheet.

____

____

____

____

____

____

____

PREPARATION OF FUSED DISKS FOR XRF MAJOR ELEMENT DETERMINATION

by

John W. Husler
Department of Geology
University of New Mexico
Albuquerque, NM 87131

First Edition: May 1988

Latest Revision: December 29, 1989

I. Preparation of Flux Mixture

Grind approximately 6 g reagent grade ammonium nitrate (NH_4NO_3) in a mullite or diamonite mortar and pestle to a fine powder. Sieving is not necessary.

Weigh out 5.04±0.0002 g of the crushed NH_4NO_3 into a 14 or 15 dram vial and add a plastic mixing ball. Add, from a full 1 lb bottle of Baker Fluxgrade (R) or equivalent grade lithium tetraborate ($Li_2B_4O_7$), enough powder to fill the vial about 2/3 full. Cap and mix in a ball mill for about five minutes.

Remove the plastic ball, dump the contents of the vial into the original one pound bottle of $Li_2B_4O_7$, cap and mix vigorously by hand for about five minutes. Use 9.10 g of this mixture (9 g $Li_2B_4O_7$ + 0.1 g NH_4NO_3) for each 1.00 g sample.

II. Preparation of Equipment for Disk Making

Preheat Corning (R) hotplate on setting of 6. Preheat Lindberg (R) box furnace to 1000±70 °C. Furnace is sufficiently hot when interior lining is red hot.

When not in use, molds and crucibles may be left in 6N HCl solution, or may be cleaned and stored under lock and key. Clean molds and crucibles by removing from 6N HCl beaker (wearing safety glasses at all times) and washing with warm soapy water, rinsing with hot tap water, and then deionized water. Do not scrub. Wipe dry with a Kimwipe (R) laboratory wipe (or equivalent).

When crucibles and molds appear dull (usually after 3-5 fusions), polish with 6 μm diamond paste. If there are scratches, use 9μm diamond paste followed by 6μm. Use paste very sparingly by applying to the bottom of the crucible or mold. Cover with a small piece of Kimwipe and polish with an appropriate large pencil eraser. Pencils are labeled 9 micron and 6 micron. Return pencils to their respective boxes. Rinse the paste from the crucibles and molds with acetone, wash with warm soapy water using a Kimwipe, rinse with hot tap water followed by deionized water and then dry by blotting with a clean Kimwipe.

III. Preparation of Sample for Fusion

Weigh 1.000±0.0001 g of -100 mesh sample onto a new piece of tared glazed weighing paper. Add 9.100±0.0001 g of flux mixture by piling on top of sample such that excess flux mixture can be removed without removing any of the sample if the ratio of 9.1 to 1.0 is exceeded. Note that only the ratio of flux mix to sample is critical, so that if exactly 1.000 g of sample is not weighed initially, a calculation can be made to determine the proper amount of flux mixture to add. This often expedites the operation by requiring only one tedious weighing.

Carefully pour the weighed powder into a 14 or 15 dram vial containing a plastic mixing ball. Tap the paper gently to remove all visible powder from the paper. Cap the vial and mix gently by hand for about 30 seconds. Mix in a ball mill for about 5 minutes, **remove the plastic ball**, place the mixture in a clean 30 mL 95% Pt-5% Au crucible, and cover. NOTE: Pt-Au crucibles and molds (as opposed to pure Pt) are used to minimize sticking of fused material.

IV. Fusion

Fuse the covered mixture in the box furnace at 1000±70 ° over a period of about 15 minutes. Place a 40 mm Pt-Au mold beside the crucible to be heated. Placement of the mold in the furnace can be delayed until the last five minutes (or so) of heating to minimize the chance of furnace particles falling into the mold. Once the sample has become molten (5-10 min), swirl the melt (using long tongs, and wearing heat-resistant gloves, safety glasses and protective clothing) intermittently to homogenize the melt.

After about 15 minutes, remove the lid, swirl the melt vigorously but carefully, and quickly but carefully pour the melt into the mold. With the tongs, grab the mold firmly by the lip and remove from the furnace.

Hold the mold just above the hotplate for about 15-30 seconds **after** the melt has cooled below red heat, then place the mold on the hotplate (metal surface down). Keep the tips of the tongs on the hot plate to avoid thermal shock to the sample when picking up the mold. Remove the disk after about 15 minutes by inverting the mold with the tongs, grabbing opposite sides of the bottom of the mold and **gently** tapping the top part of the mold on the hot-plate. Keep the rim as flat as possible so as not to bend the mold in any way.

Glasses which are stubborn in separating from the mold may require a longer waiting period on the hotplate, or removal from and replacement on the hotplate one or more times. In extreme cases, the melt will have to be discarded and leached from the mold with 6N HCl and the mold polished to a greater degree before fusing another split of the sample.

When molds and crucibles are cool, dump loose melt fragments in waste beaker and **carefully** set molds and crucible in beaker of 6N HCl to leach. Cover the beaker. (Do not try to scrape solidified glass melt from crucibles or molds, or try to bend crucibles or molds to remove melt residues.)

V. For Samples Suspected to Have High Organic Content

1. Accurately weigh (±0.0001 g) about 2 grams of sample in a (clean, tared) platinum crucible.

2. Ignite the sample by heating in the crucible for 1 hour at about 450 °C, then increase temperature to 800±50 °C and continue heating for another hour.

3. Reweigh the sample (in the crucible), calculating the fraction of sample lost by difference.

4. Remove the sample (now ash) from the crucible with a rubber policeman and gently grind with a Diamonite (R) mortar & pestle (no need to sieve) and accurately weigh out an amount of material equivalent to 1.0000 g of sample in its pre-ignition state (i.e., if sample weight loss fraction is 0.2 or 20%, weigh out 0.8000 ± 0.0001 g of ignited sample).

5. Prepare the fused disk as discussed in Section III above using 9.1000 ± 0.0001 g of flux mixture. (This correction procedure assures that the post-ignition weight of sample will contain the same elemental amounts as the full 1 gram of pre-ignition sample.)

ANALYTICAL METHODS FOR THE DETERMINATION OF MAJOR ELEMENTS IN ROCKS USING ATOMIC ABSORPTION SPECTROPHOTOMETRY

by

John W. Husler and James R. Connolly
University of New Mexico
Department of Geology
Albuquerque, New Mexico 87131

First Edition: December, 1988

Latest Revision: December 29, 1989

1. INTRODUCTION

This document describes step-by-step procedures used in the analytical geochemistry laboratory to determine major elements in rock samples using atomic absorption spectrophotometry (AA). The procedures discussed herein apply to most igneous, metamorphic and sedimentary rock samples. Although the procedures are quite detailed, considerable operator expertise and experience are required to produce consistently high quality analyses. Analysts new to AA at UNM will need to work closely with John Husler to learn these procedures in a hands-on setting. Some of the procedures used in this laboratory differ somewhat from those which experienced AA analysts may have used in other labs.

The procedures are presented in four sections. Section 2.0 describes the procedures to be used to prepare the sample and standard solutions to be analyzed by AA. Section 3.0 describes the procedures to be followed for startup and shutdown of the Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. Section 4.0 outlines the steps to be followed to gather and record the data. Section 5.0 describes the procedures to be used to analyze the data and calculate weight percents of the elements determined.

These procedures have been developed and refined over 20 years by the senior author (Husler); many have been outlined in various "in-house" documents developed as instructional and operational aids. This manuscript was developed in response to the need to document analytical procedures for work to be performed in the Department of Geology at the University of New Mexico (UNM) for the Yucca Mountain Project (YMP) under contract to Sandia National Laboratories. It is designed, in conjunction with other Technical Procedure documents in which it is incorporated, to partially meet the requirements for Quality Assurance connected with this YMP work.

Values for expected errors in the measurements outlined in these procedures assume that Class A laboratory glassware (burets, volumetric flasks, etc.) is used for all measurements, as required for YMP work. Unless otherwise stated, the ± amounts given as estimated variation in measurements are those values assumed for the laboratory standard as defined by ASTM (TP-61, Table 1). Estimated errors in sample weights are based on annual calibration data for the Mettler (Brand) balance used for all YMP work.

2.0 PREPARATION OF REAGENTS AND SAMPLE AND STANDARD SOLUTIONS

2.1 Overview

Many special preparation procedures for samples, standards and reagents are used to assure that all solutions are prepared identically. All solutions of standards and samples are prepared at the same time and place, using reagents prepared in identical lots under the same environmental conditions (i.e., temperature, humidity, etc.). This eliminates variations in the solutions other than those due to sample composition and assures high-precision results without requiring extreme accuracy in sample-independent measurements. Samples may be prepared while the AA is warming up (Section 3.0).

2.2 Preparation of Cesium-Hydrochloric Acid (Cs-HCl) Reagent

Cesium is added to the hydrochloric acid reagent used in the analyses to minimize ionization interference in the flame. Sufficient quantity of the reagent must be available so that all standard and sample solutions are prepared with the same reagent solution, eliminating inaccuracies that might be caused by variation in the composition of the reagent.

If sufficient reagent is not on hand, prepare Cs-HCl reagent by dissolving 24.34±0.002 g of Beckman (Brand) scintillation grade CsCl (or equivalent) in 4.0±0.008 L of 1:1 HCl and mixing thoroughly. (Always use caution when using concentrated acids). Whether using on-hand or newly prepared reagent, prior to preparing samples, standards and blank: 1) flush some reagent through the automatic dispenser [Repipet(R)], 2) mix with the larger volume of reagent, and 3) transfer some reagent back to the Repipet. This insures homogeneity of the reagent. Store excess reagent in a polyethylene bottle.

2.3 Preparation of Samples and Standards

Several different reagents are used in the following preparation, including 1% HNO_3, 1:1 HNO_3, 48% HF, 1:1 $HClO_4$, and Cs-HCl reagent. The acids are reagent grade and dilutions are made with deionized water. Be certain there is enough of each reagent, including deionized water, to complete the entire set of samples and standards, including dilutions (see below), from the same batch of reagents. Sufficient quantity of cleaned 100 mL volumetric flasks and 125 mL Polyethylene bottles (See Section 2.5) should be available to hold all solutions prepared.

Weigh 0.2±0.0001g of -100 mesh powdered sample on a new piece of tared, glazed weighing paper. Handle the paper only with tweezers or gloves. Carefully transfer the sample to a 100 mL Teflon beaker containing 1-2 mL of 1% HNO_3. Rinse any powder adhering to the paper into the beaker with 1% HNO_3 from a polyethylene wash bottle, swirling solution in the beaker. Weigh exactly 0.1, 0.2 and 0.3 g (all ±0.0001g) of suitable rock standard, and prepare solutions in the same manner, using the same reagents under the same conditions. Standards may be a NBS or USGS rock standard, or any suitable in-house rock standard which has been previously standardized against a nationally or internationally recognized rock standard. Also prepare a blank (with all reagents but without any sample or standard material) in the same manner to run through the entire procedure with samples and standards.

Each Teflon beaker used in the laboratory has an identification mark (letter, number or other symbol) permanently etched onto its exterior. In a laboratory notebook, for each sample, standard, and blank prepared, record the following: the beaker ID mark, laboratory ID for samples, ID for standard solutions, weight of sample or standard used, tare weight of paper and any comments.

Cautiously, under a fume hood, wearing protective glasses, gloves and lab coat, add 10 mL 1:1 HNO_3, 15 mL 48% HF, and 5 mL 1:1 $HClO_4$ to each sample, standard and blank, then evaporate to dryness on a hot plate. Exact amounts of the acids are not required; measurements are done using graduated cylinders and are accurate to about ±0.2 mL. The evaporation must be performed at a temperature low enough to prevent the beaker from adhering to the hot plate. This temperature is approximately 200 to 250 °C, but precise temperature setting is not required; it merely must be sufficient to evaporate the solution. A few droplets of liquid remaining on the walls of the beaker are of no consequence.

Cool the residue, add 20±0.2 mL Cs-HCl Reagent (see Section 2.2 for preparation procedure) to the beaker using an automatic dispenser such as a Repipet. The Repipet is used to deliver a preset amount of solution with ±0.1% precision and 1.0% absolute accuracy; the same preset amount should be used for each solution of sample, standards and blank prepared for analysis. Warm sample on a hotplate (about 60-80°C) to dissolve the salts and transfer to a 100 mL volumetric flask, carefully rinsing all material from the beaker with deionized water. Cool to room temperature (by letting samples stand a few minutes) and dilute to 100±0.08 mL with deionized water. To avoid volume errors due to room temperature variations, dilute the blank, standards, and samples at the same time.

2.4. Preparation of 1:10 and 1:100 Dilutions

Pipet 10±0.02 mL of each sample, standard and blank solution into separate 100 mL volumetric flasks. Add, with automatic dispenser (i.e., Repipet), 18 mL (see Sec. 2.3 for precision and accuracy values) of Cs-HCl reagent, then dilute the solutions in each flask to 100 mL with deionized water.

In cases where the elemental concentration in the 1:10 dilution of the sample is expected to exceed the highest standard (and a more suitable standard is not available), 1:100 dilutions of sample may be prepared from a portion of the 1:10 dilution. Preparation is identical to that detailed above (including the appropriate addition of 18 mL Cs-HCl reagent to keep the Cs content constant in all solutions). The 1:100 dilutions are required only for determination of very high-concentration elements, such as Ca in a carbonate rock.

2.5. Transfer Solutions to Polyethylene Bottles

Upon diluting and mixing, the solutions are transferred to 125 mL polyethylene bottles. Generally, the solutions are aspirated into the AA flame from these bottles; if analyses are done on the same day as the solutions are prepared, 1:10 solutions may be aspirated from the 100 ml flasks, and transferred later into bottles. The precise time of the transfer is not critical as long as all solutions (samples, standards and blank) are transferred at the same time and place.

Only bottles and flasks which are used for whole-rock AA samples are used; this avoids possible contamination by bottles which have had other solutions in them. Prior to use, the polyethylene bottles (and all glassware) are washed in a hot Alconox (Brand) detergent - tapwater solution, rinsed with hot tap water and then with deionized water. Bottles are then rinsed with 6N HCl, followed by hot tap water, and 4 rinses in deionized water.

3.0 STARTUP/SHUTDOWN OF THE P-E MODEL 303 AA SPECTROPHOTOMETER

Samples, standards, and blank are prepared as detailed above. For determinations of elements in rocks such as basalts, rhyolites, granites, and andesites (and many other silicate rocks), use the optimum instrument parameters listed in Table C-1. For determinations of elements not in Table C-1, consult the Perkin-Elmer (P-E) methods book for proper instrument settings, standard concentrations and references.

1. **IMPORTANT: FAILURE TO OBSERVE THE FOLLOWING PRECAUTIONS IS LIKELY TO CAUSE A DANGEROUS EXPLOSION!!** Wear safety glasses. Be sure there is water in the drain loop and that the drain tube is immersed in water. Be certain proper burner is fastened in place and proper gasses are connected. Ensure that the proper gasses are connected (NEVER use oxygen!) and that the proper burner is in place.

For $N_2O-C_2H_2$ (nitrous oxide - acetylene) flames, use ONLY the FLAT single slot burner. Use of any other burner will probably cause an explosion.

For Air-C_2H_2 flames, a) the cylindrical, single slot or b) Boling 3-slot burner heads are generally preferred, although the flat single slot head may be used also.

2. Make sure fan in fume hood is on. Switch for fume hood is in Room 215, north wall.

3. Make sure source knob (lower right knob on left front panel) is turned down (fully counter-clockwise).

4. Install proper cathode tube or EDL (electrodeless discharge lamp) for first element to be determined. Cathode tubes and EDLs are in cabinet in alphabetical order by their elemental symbol.

EDLs are not used for routine determination of elements in whole-rock analyses.

5. Plug in instrument and chart recorder power supply (if not already plugged in).

6. Turn power switch on left front panel on, and turn on chart recorder power supply. Make sure the chart recorder knob is on AMP (standby position). Allow instrument to warm up a minimum of 30 minutes. This can be done while sample and standard preparation is being completed.

7. Set filter, slit, and range (left front panel) on recommended settings for the particular element being analyzed (Table C-1).

8. Set cathode current to value appropriate for the cathode tube being used by adjusting the source knob while observing the current meter in the lamp compartment above the left front panel: for lamps specifying a maximum and an operating current, set current to the operating current. For lamps specifying only a maximum current, run at approximately 90% of the maximum. Precise setting of sample current is not required, but **NEVER, UNDER ANY CIRCUMSTANCES, EXCEED THE MAXIMUM RATING FOR EACH CATHODE TUBE.**

9. Meter Response, Scale, Zero, and Null Meter (absorption) knobs on the instrument itself are not used when using the Chart Recorder (see Item 13), and settings need not be changed.

10. Set the wavelength counter to the approximate wavelength by adjusting the coarse wavelength control and finally peak the wavelength with the fine wavelength control. Proper adjustment is attained when the energy needle deflects as far to the right as possible. If the energy needle is off scale, it can be adjusted with the gain control. Check the position of the cathode tube so that it, too, causes maximum deflection of the energy needle to the right. Finally, clamp the cathode tube down, adjust the energy needle with gain control so that it is in the black area, and close the compartment.

11. If the vernier on the left of the burner post is in the middle of the "2" (it almost always is), adjustment is not necessary. If necessary, the burner height is adjusted by first setting the null meter on scale with the zero knob. The burner is

next raised (by lifting the level under the burner while holding the knob on the lower right of the burner) until the burner head blocks out the light in the path as noted by deflection of the null meter. Finally lower the burner about 1 cm below the light path.

NOTE: If the strip chart recorder is being used, the burner height adjustment is made by observing deflection of the recorder pen instead of the null meter.

12. Ignite burner. Use A or B depending on mode of operation to be used. Always follow shutdown procedures (Section 14) when changing fuel mixtures, or explosions and severe damage may result.

A. Operation with Air-C_2H_2:

1. For Air-C_2H_2 **ALWAYS TURN THE AIR ON FIRST AND OFF LAST.** Before proceeding, make sure that compressed air supply (in-house or compressed air tank) is connected to the "Air In" on the back of the P-E Burner Regulator Box and all fittings are tight. Note that the same "Air In" line is used for N_2O when it replaces air as the oxidant. This means that the line must be switched if N_2O was used for the previous analysis.

2a. If using in-house compressed air: Turn on air valve (slowly!) until valve is parallel to the line. Flow rate should be about 30 psi on Air Flow meter; adjust with AIR control if necessary. If sufficient pressure cannot be obtained, check the in-house pressure: Open air flow valve (black knob to left of main air valve) until top pressure gauge reads a maximum value (usually about 40 psi). If pressure is not at least 32 psi, use compressed air. If pressure is sufficient, then close this valve until pressure reads about 2 psi less than the maximum value.

2b. If using compressed air tank: On the air tank, back-off (counter-clockwise) the key-type regulator knob a few turns until loose. Slowly turn on main air tank valve (counter-clockwise) and tighten regulator knob (clockwise) until outermost gauge on regulator (closest to line fitting) reads approximately 40 psi. (NOTE: The compressed air tank is used only in those rare instances when the in-house compressor is not operating.)

3. Adjust air flow meter knob (on top of Burner Regulator Box above air flow float gauge) if necessary to achieve a reading of about 9 on the air flow meter.

4. Lift up (open) C_2H_2 safety valve on right top of P-E Burner Regulator Box.

5. On the C_2H_2 tank back-off (counter-clockwise) the C_2H_2 regulator key-type knob a few turns. Turn on main C_2H_2 cylinder valve (counter-clockwise) slowly several turns and adjust regulator knob (clockwise) until outermost gauge on regulator (closest to line fitting) reads approximately 9 psi. If the main regulator gauge (closest to cylinder valve) registers less than 50 psi, the tank should be changed (C_2H_2 fitting in gauge to cylinder is **left**-handed.)

6. Adjust flow rate on Fuel Flow meter (by adjusting Fuel Flow float valve on P-E Burner Regulator Box) to about 9 psi. Fuel float gauge is read using the center of the white (upper) ball. Flip down C_2H_2 safety valve until ready to light burner. Recheck water in drain loop and reservoir.

7. Ignite burner using either LAB LYTER (R) or long striker. Make minor adjustments to fuel (C_2H_2) flow to obtain a blue (fuel-lean) flame which is used for most elements. This is best achieved by increasing the fuel flow until the flame becomes slightly yellow, and then decreasing the fuel flow until the yellow just disappears.

B. Operation with N_2O-C_2H_2:

1. For N_2O-C_2H_2, **ALWAYS TURN THE N_2O ON FIRST AND OFF LAST.** Before proceeding, make sure that N_2O gas cylinder is connected to the "Air In" on the back of the P-E Burner Regulator Box and all fittings are tight. See A.1. above.

2. Plug in N_2O heater in outlet on post by the cylinder.

3. On the N_2O tank, back-off (counter-clockwise) the key-type regulator knob a few turns. Slowly turn main N_2O cylinder valve on (counter-clockwise) and adjust regulator

(clockwise) until outermost gauge on regulator (closest to line fitting) reads 60 psi.

4. Air pressure gauge on P-E Burner Regulator box should read about 30 and air flow meter should read about 9. Adjust air float meter knob (on top of box above air flow float gauge) only if necessary.

5. Lift up (open) C_2H_2 safety valve on right top of P-E Burner Regulator Box.

6. On the C_2H_2 tank, back-off (counter-clockwise) the C_2H_2 regulator knob a few turns. Turn on main C_2H_2 cylinder valve (counter-clockwise) and adjust regulator (clockwise) until outermost gauge on regulator (closest to line fitting) reads 9 psi.

7. Adjust flow rate on Fuel Flow meter (by adjusting Fuel Flow float valve on P-E Burner Regulator Box) to 9 psi. Fuel float valve is read using the center of the stainless steel (lower) ball. (White plastic ball will probably not be visible.) Flip down C_2H_2 safety valve until ready to light burner (next step). Recheck water in drain loop and reservoir.

8. Ignite burner using either LAB LYTER (R) or long striker. Make minor adjustments to fuel flow to obtain, as a first approximation, a flame in which the crimson edge or "feather" extends about 1/2 to 1 cm above the burner. Set, depending on element, as outlined in Section 4.0-2.b.

9. Remember that the flip valve on top of the regulator box is a **safety** valve; it should always be flipped down (off) if/when the burner begins to sound strange or fuel or oxidant levels begin to cause a change in flame characteristics.

13. Setup of the Perkin-Elmer Model 165 Chart Recorder.

NOTE: The procedures listed below are followed for each element determined, and after any changes in cathode tubes, burners and fuel mixtures are complete. When setting up recorder, make sure burner has been operating for at least 2 minutes.

A. Make sure Model 165 recorder power supply is on, the recorder set to AMP and has warmed up for at least 30 minutes.

B. Prepare the P-E Model 303 as detailed in previous sections, then perform the following steps while aspirating (See Section 4.0 - 2) deionized water into the flame.

C. Remove protective parafilm or rubber piece from chart pen. On the recorder readout module, set the noise suppression on 2, and the scale expansion on x1.

D. Turn the recorder knob to SERVO and adjust pen to zero (right hand base line) with the FULL SCALE Knob.

E. Block out the light at the window on the right hand side of the flame (using the card between the AA and the recorder) and adjust the pen to 100% by raising the recorder lid and adjusting the ZERO knob.

F. Remove the card and repeat steps D and E until blocking and unblocking the light path causes no notable shift in the zero and 100% positions. NOTE: While analyzing samples, this process may be done with the prepared blank instead of deionized water, which sets "baseline" conditions for the samples to be analyzed. In this case, aspirating deionized water would usually cause the needle to deflect to the right of the zero line. In most cases (especially with elements which are prone to drift), it is best to zero with water and subtract out the baseline data for the blank.

G. Turn the chart speed knob to the desired rate (usually 60 mm/min.). Do not use a speed of less than 60. Turn the RECORDER knob to CHART.

H. When chart expansion is required, place scale expansion knob (on recorder read-out module) on desired range. Adjust instrument to zero on baseline using deionized water (or on blank for sample analysis) with the ABSORPTION RANGE Knob. Do not change the FULL SCALE knob as it has previously been set on x1 scale.

I. When finished recording data (Section 4.0) or whenever a change of fuels or burner is required), proceed to shut down procedures.

14. Shut-down of the Instrument
(NOTE: The order of gas shutdown is **very** important.)

A. Remove capillary tube from distilled H_2O (do not draw H_2O unless flame is lit).

NOTE: If merely changing between Air and N_2O during a series of elemental analyses, **flip down (close) the C_2H_2 safety valve**, turn off the oxidant (D below) and change burner heads (if necessary). See section 3.0 for discussion of appropriate burners. Connect and begin flow of the appropriate oxidant, reopen the C_2H_2 safety valve and light the burner following the steps given above. Note that for switching from N_2O to air, the fuel flow must be reduced to about 9.0 with the **white** (upper) ball on the fuel flow meter on the P-E Burner Regulator Box. For final shutdown, proceed with the following.

B. Flip C_2H_2 safety valve down (off) on P-E Burner Regulator Box.

C. Turn off main C_2H_2 valve on cylinder (clockwise), open (flip-up) C_2H_2 safety valve on burner regulator box (to bleed the line of all C_2H_2), back-off (counter-clockwise) acetylene regulator key-type knob and re-close (flip-down) the C_2H_2 safety valve.

D. If using air as the oxidant, turn off main air valve (turn handle perpendicular with air line). If using N_2O, turn off main N_2O valve on cylinder (clockwise), allow the line to bleed off N_2O, then back-off regulator key-type knob (counter-clockwise) a few turns until loose; unplug the N_2O heater.

E. Turn source knob down (fully counter-clockwise).

F. Turn off power switch on recorder.

G. Turn off power switch on the Model 303.

H. Make sure pen is protected from drying out by placing parafilm or rubber piece between pen and chart paper. If pen dries out, a small piece of piano wire (in spare parts drawer) will be necessary to unplug pen. Cover recorder.

I. Clean up the area.

4.0 DATA COLLECTION USING CHART RECORDER

To minimize changing of burners and the amount of time used to collect data, elements requiring the use of C_2H_2-Air mixtures are run first, followed by all those requiring C_2H_2-N_2O mixtures. Within each run for an element, standard solutions appropriate for the element of interest are run first, followed by groups of 3 to 5 samples alternating with the standard solutions. Following completion of all sample runs, standards are run a final time.

For concentrations found in rock types listed in Section 3.0, Al, total Fe, Ti, Mn, Sr, and Ba are usually analyzed directly using the undiluted blank, standards and samples. Solutions are retained after analysis for the colorimetric determination of phosphorous. Ca, Mg, Na, and K are usually analyzed on the 1:10 dilutions of samples and standards. For very low concentration elements (typically Mn, Ba), undiluted sample solutions may be analyzed against 1:10 standards. For elements present in extremely high concentrations, 1:100 dilutions may be used and analyzed against the 1:10 standards.

The step-by-step data collection procedures are outlined below:

1. The AA should be operating with the proper fuel and cathode tube and setup as described in Section 3.0 (including preliminary setting of background to zero and full scale to 100 percent absorption). Chart recorder speed may be adjusted as necessary (but never to less than 60).

2. Adjust Flame. All solutions are aspirated into the flame by placing the thin aspirating tubing (connected to the center fitting of the burner-nebulizer unit) into the polyethylene bottle, flask or beaker containing the solution. Always wear safety glasses and gloves while handling solutions and working on or near the AA.

   a. For elements in Table C-1 determined with air-C_2H_2, adjust the flame (while aspirating deionized water) for the element to be run with the fuel flow knob until the yellow color just disappears.

b. For elements determined with $N_2O-C_2H_2$, the flame must be adjusted while aspirating a sample or standard; with the chart recorder on, adjust fuel flow to the point where maximum absorption (deflection to left of recorder pen) is attained, but away from any setting where a slight change in the fuel rate causes a noticeable change in absorption. Recheck background to insure that maximum absorption was not merely a shift in background level. Crimson feather should be from 1/2 to about 10 cm high. Do not allow the flame to become too fuel-rich or too fuel-lean.

NOTE: This $N_2O-C_2H_2$ adjustment varies from element to element, but is especially critical with titanium. Ca, Mg, Fe, Sr, and Ba may be analyzed with Air-C_2H_2, but under the conditions of this method, accurate results for most rock samples can only be reliably obtained with $N_2O-C_2H_2$ due to matrix interferences with the cooler Air-C_2H_2 flame.

3. Set up strip chart as detailed in Section 3.0 (Item 13). Zero and 100% absorption are checked and reset for each element determined. The first readings on each strip chart will be these settings. At the beginning of each run for a particular element, label the strip chart with the element being determined, the laboratory sample ID, the organization providing the sample, the date, and the initials of the analyst. Note any variations in setup parameters from those outlined in Table C-1 (i.e., burner used, dilution factor, etc.).

4. With recorder set to desired chart speed for analysis, aspirate deionized water, the blank, and the various concentrations of standard solutions so that each deflection peak is recorded. Dilutions appropriate to the element being analyzed (Table C-1) are used. Aspirate the solutions until a flat absorption peak is obtained. Label each peak on chart with the laboratory ID, solution concentration, and dilution. Also note any variation in the scale setting from the parameters given in Table C-1.

5. Next aspirate 3 to 5 sample solutions, labeling each peak with the lab ID and dilution, and any variations as in 4 above.

6. Repeat steps 4 and 5 above for groups of samples until all samples have been aspirated and data recorded. Whenever high accuracy is required, always run the standard solutions a minimum

of three times for each element. The final run on each chart is always a run of standards and blank. Do not use data where samples or standards exceed 90% absorption (on x1 scale); these should be rerun using more dilute solutions.

7. Chart may be advanced and data removed from recorder. Between runs, turn chart recorder to AMP (standby position).

The steps above are repeated for each element to be analyzed.

5.0 DATA ANALYSIS: CALCULATION OF AMOUNTS OF ELEMENTS DETERMINED

Data collected on the strip charts (Section 4.0) are analyzed graphically to determine the amounts of each element present (reported in oxide form). Data for each element are analyzed using standard curves relating percent absorption and concentration prepared for that particular run.

Step-by-step procedures followed for each element analyzed are outlined below:

1. On the strip charts, read and note the position of each absorption peak (blank, standards, and sample); data read are percent absorption, with 1 division equal to 1%. (This will always be true unless 3X or 10X chart expansion is used.) Scale divisions on the chart paper are read to ±0.1 division on the flat part of the peak. (Figure C-1 is a copy of a typical strip chart.) NOTE: If the zero has been set on the strip chart with the blank (instead of deionized water) the blank reading should be zero. If zero has been set with deionized water, the blank reading should be zero or some small non-zero value.

2. Check the chart for drift by comparing the peak values for the standards throughout the run. Drift is defined as a progressive change over time of absorption, determined by successive measurements of the standard solutions. Drift can be either upward or downward over time.

   a. A systematic (constant direction) change of more than 1% (1 division) is considered drift, and should be compensated for in the data reduction. A series of straight lines are drawn connecting each of the 0.1, 0.2, and 0.3 g standard peaks and the blank peaks on the strip chart and used for drift correction.

b. For most elements, a non-systematic change of less than ±1.5% is considered acceptable random error and the values are averaged.

c. Non-systematic change of more than ±1.5% indicates unacceptable random error; data should be discarded and samples rerun.

3. Standard curves are prepared by scaling element oxide concentration in the rock standards (abscissa) vs. percent absorption (ordinate) on inverted 1 cycle x 60 divisions semi-logarithmic graph paper. The abscissa is scaled with 0% at the origin at any convenient scale to include about twice the amount present in the rock standard. The origin is set equal to 0%, and the 0.2 g standard solution is set equal to the element oxide concentration in the rock standard (thus the 0.1 g and 0.3 g solutions equal 0.5 and 1.5 times the rock standard amounts, respectively).

Since sample and standard solutions are prepared in exactly the same manner, letting the 0.2 g standard represent the actual concentration of the respective oxide in the rock allows direct plotting of sample concentrations. For example, if the CaO content of the rock standard is 6.00%, the 0.1, 0.2, and 0.3 g standards will represent 3.0, 6.0 and 9.0% CaO, respectively, on the standard curve.

4. For low-concentration samples in which scale expansion on the strip chart recorder of 3X or 10X is required, the same procedures are followed as in item 3 above, except that linear graph paper is used for ordinate and abscissa. (This is because at low concentrations, Beers Law relating absorption to concentration is approximately linear.)

5. Actual plotting and reading of the standard curves to determine amounts in the samples is slightly different depending on the magnitude of drift.

a. If drift correction is not required, connect the points defined by the blank (0% concentration) and the three standard concentrations, using the average of all runs. These points will be slightly convex upward (due to increasing self absorption in higher concentration solutions); a flexible 18" x 1/4" spline curve made from 1/8" thick PVC (designed by John Husler) is used to connect the points.

Plot the percent absorption values for the samples on the ordinate, and read the sample concentration on the abscissa. For undiluted 0.2 g sample solutions, this value is the weight percent of the oxide in the sample. If lower concentration solutions are run against the undiluted standards, this value is corrected appropriately.

b. If the drift over time is less than or equal to 2% (2 scale divisions), prepare two standard curves, one for the first values and another for the final values; label the curves. In cases where extreme precision is not required, this method may be used for runs where drift exceeds 2%.

Sample percent absorption (minus blank if appropriate) is read from the strip chart, and concentration is read on the abscissa, with the point read interpolated between the high and low standard curves based on the time the sample data was collected relative to the standards. If lower concentration solutions are run against the undiluted standards, this value is corrected appropriately.

c. If the drift over time is greater than 2% (2 scale divisions), standard curves are plotted for each sample based on the drift. Make drift curves for each of the standard solutions by connecting drifted peaks on the strip chart. Read the percent absorption for the drifted peaks at the position of each sample peak, and plot an absorption-concentration curve for that sample (as in 5.a. above).

Plot the percent absorption values for the samples on the ordinate, and read the sample concentration on the abscissa. For undiluted 0.2 g sample solutions, this value is the weight percent of the oxide in the sample. For lower concentration solutions, correction is made as in 5.a. above. For economy in use of graph paper, absorption-concentration curves for several samples may be overlaid on the same piece of graph paper.

Table C-1

ATOMIC ABSORPTION PARAMETERS FOR ANALYSIS OF SILICATE ROCKS

Note: For cathode current setting, use current recommended on lamp. If no operating current is listed, use 90-95% of maximum. Do not exceed the maximum in any case. In table below, l is wavelength in nano-meters (nm).

Oxide	l(nm)	Approx. l Dial Setting	Slit	Range	Filter	Fuel	Oxidant	Burner	Scale	Dilution
Al_2O_3	309.3	309	3 (0.3mm; 2 Å)	U. V.	out	C_2H_2	N_2O	N_2O (7 cm, flat)	1X	none
Fe_2O_3	248.3	248	3 (0.3mm; 2 Å)	U. V.	out	C_2H_2	N_2O	N_2O (7 cm, flat)	1X	none
MgO	285.2	285	3 (0.3mm; 2 Å)	U. V.	out	C_2H_2	N_2O	N_2O (7cm, flat)	1X	1:10
CaO	422.7	211	3 (0.3mm; 2 Å)	VIS.	out	C_2H_2	N_2O	N_2O (7 cm, flat)	1X	1:10
Na_2O	589.0	294	4 (1mm; 13 Å)	VIS.	out	C_2H_2	AIR	1-slot (Round)	1X	1:10
K_2O	766.5	383	4 (1mm; 13 Å)	VIS.	in	C_2H_2	AIR	3-slot (Boling)	1X	1:10
TiO_2	364.3	364	3 (0.3mm; 2 Å)	U. V.	out	C_2H_2	N_2O	N_2O (7 cm, flat)	3 or 10X	none
MnO	279.5	279	4 (1mm; 7 Å)	U. V.	out	C_2H_2	AIR	3-slot (Boling)	3 or 10X	none
SrO	460.7	230	3 (0.3mm; 4 Å)	VIS.	out	C_2H_2	N_2O	N_2O (7 cm, flat)	3 or 10X	none
BaO	553.6	277	3 (0.3mm; 4 Å)	Vis.	out	C_2H_2	N_2O	N_2O (7 cm, flat)	3 or 10X	none

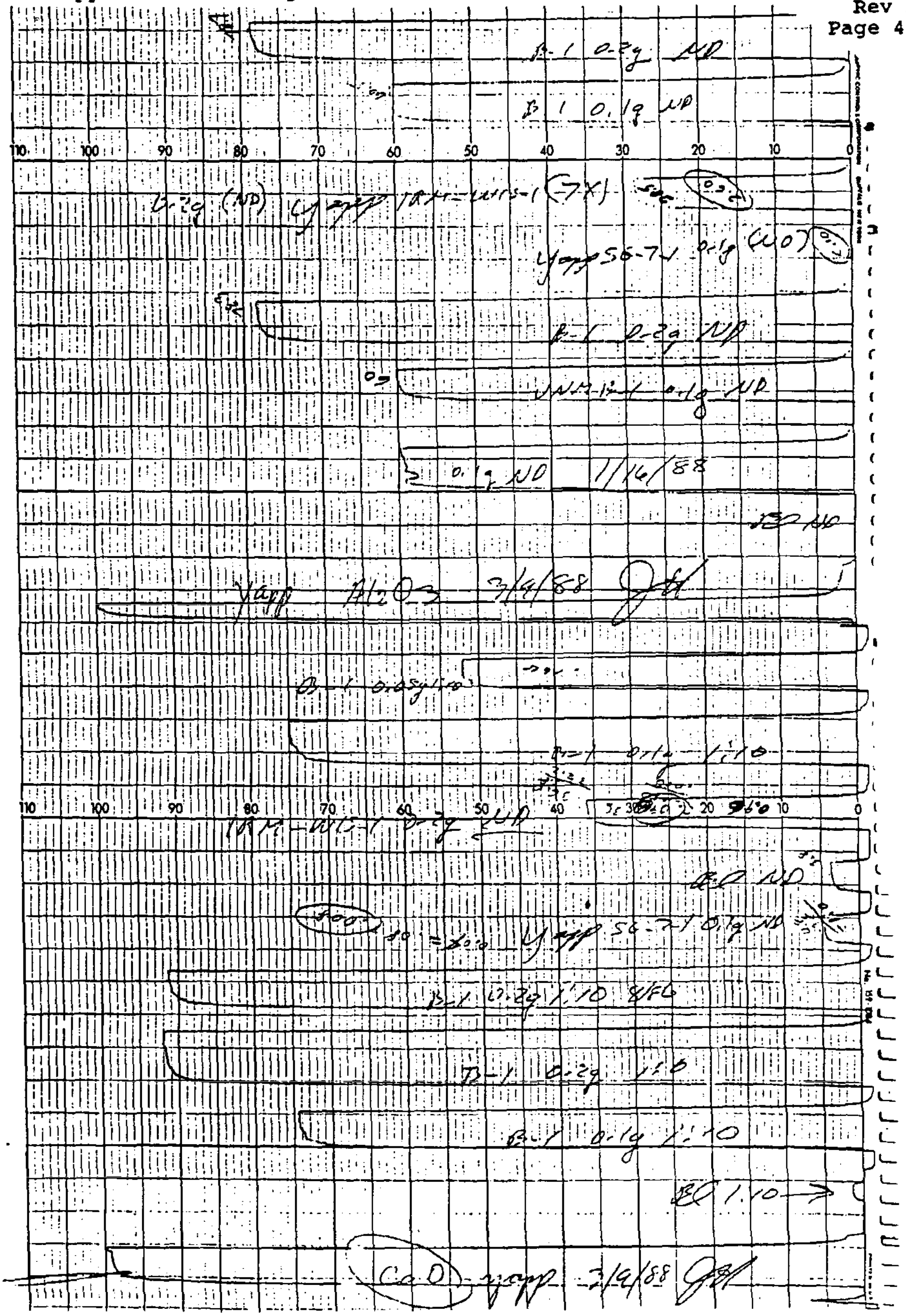

Figure C-1: Copy of typical strip chart from atomic absorption spectrophotometer.

OPERATION OF THE RIGAKU 3064-M X-RAY FLUORESCENCE SPECTROMETER

by

Richard Abitz
(with modifications by John Husler and Jim Connolly)
University of New Mexico
Department of Geology
Albuquerque, New Mexico 87131

First Edition: February 24, 1988
Last Revised: December 29, 1989

PART A. Gas Flow in Proportional Counter (For Major Element Analysis **only**--Skip this step if doing trace element analyses)

1. Check P-10 gas cylinder behind XRF. The round left gauge should read approximately 40 kPa. If necessary, adjust with the large black knob below the gauge, first making sure rectangular flow meter is off (silver knob fully clockwise).

2. Adjust rectangular flow meter to read 0.10 SCFH air (metal ball is visibly level with 0.10 on scale). Check and re-adjust 5-10 minutes after first turned on, at least one hour before calibrating the flow proportional counter.

NOTE: If pressure on right cylinder gauge is below 1000 kPa when starting up, the P-10 gas cylinder should be exchanged. Follow the steps outlined below:

a. Loosen (in counter-clockwise direction) the large black knob before closing the main valve. About 4-5 turns are sufficient. Do not loosen too far or the knob will fall off. Loosening protects the regulator gauge, the flow meter, and the flow proportional counter window.

b. Close the flow meter valve by turning the small silver knob on the front clockwise. The ball will drop to zero.

c. Turn off (clockwise) the main cylinder valve.

d. With crescent wrench, disconnect the gauge from the cylinder. The brass fitting is a left-hand thread, and is removed by turning **clockwise**. Hold the gauge in the left hand while loosening to prevent it from swinging down and hitting the tank.

e. After putting the new full cylinder in place, remove cap, thread the fitting of the gauge back on the full cylinder and tighten snugly with the wrench. Remember, this is a left-hand thread and is tightened by turning **counter-clockwise**.

f. Place cap on empty cylinder and label cylinder EMPTY. **Chain all cylinders to the wall.**

g. **Make sure the black regulator knob is still loose before slowly cracking open the main (top) cylinder valve. Open the valve 2-3 turns.**

h. **Slowly adjust the large black knob to 40 kPa and proceed with step 2 above.**

PART B Warm-up (major and trace element analysis)

This instrument produces X-RAYS. Although all modern safety devices are installed, don't depend on them-follow directions:

1) Is x-ray light located on top of machine on? If not, consult the staff chemist (John Husler).

2) If x-rays are being generated (x-ray light is on), proceed by referring to the switches and knobs located on the upper-right panel of the instrument:

   a) Locate the kV and mA knobs below the tube voltage/current meters. Increase the settings slowly in increments of 5 kV and 5 mA (at least 15 seconds at each setting), keeping the kV value greater than the mA value at all times. Final settings: 50 kV, 45 mA.

   b) Check Load knob, should be set at 3.

   c) Let x-ray power supply stabilize for 15-20 min.

PART C Prepare and Load Samples

NOTE: It is most convenient to prepare and load your samples while slowly adjusting the kV and mA on the instrument (PART B, Item 2.a.).

Remove sample holders and the appropriate standard(s) from the desiccator cabinet. Place fused disks or pressed pellets into the holders; **do not touch the sample surface with your fingers.** Be sure the sample holder caps are threaded correctly (cross-threaded holders will jam in the sample chamber) by observing the threads and comparing the height of each holder to the standard. If cross-threaded, seat cap correctly by turning it counter clockwise several turns and then reseat by turning clockwise.

A maximum of five samples can be analyzed in a single run. The sample holder can hold six samples, but the first position is always reserved for the intensity reference: BCR-1 for major elements; SY-2 for Rb, Sr, Y, Zr, Nb; MRG-1 for Cr, Co, Ni, Cu, Zn; G-2 for Ba; GSP-1 for Hf. In some cases another standard may be inserted and run as a sample. (If doing major elements and counters have not been calibrated, load the CALIB standard instead of the intensity reference in position 1--See Part D below.)

To load samples:

1. Open sample chamber by turning the large silver handle counter-clockwise. When gate valve has closed and chamber vented, you will be able to open the door. Make sure the toggle switch below the sample chamber door is ON ("up"); it must be on for the sample to advance.

2. Place the intensity reference (or CALIB) standard in position 1, and all other samples in other positions. Always fill up lowest numbered positions; if loading less than 6 samples, leave the highest numbered positions empty. Press the black button (next to door) to advance to next position. If the holder jams after pressing the button, quickly turn off the toggle switch, remove the sample holder, and rethread the cap or reposition the holder. After loading your last sample (before closing the door) press the black button once more to make sure samples are seated properly.

3. Enter date, name of analyst, type of analysis (e.g. major elements, Rb-Nb, Ba, etc) sample #'s and positions in log book.

4. After all samples are loaded and logged, close the door and turn handle clockwise. Proceed when green vacuum shutter and vacuum lights on microprocessor panel are illuminated.

PART D Calibration of Scintillation and/or Proportional Counters

1. Check that gas level gauge on P-10 cylinder is stable at 0.10. If not, reset and wait 15 minutes to stabilize flow. (This is for major element analysis only.)

2. Make sure tube voltage and current are set at 50 kV and 45 mA. If not, reset and wait 15 minutes to stabilize X-ray tube.

3. The sample holder marked CALIB (found in desiccator cabinet on counter) should be in position 1 in the sample chamber (See Part C.2). The PHA windows of the two detectors (scintillation counter and gas flow proportional counter) are set with the Mica-Fe (fused disk) regardless of the type of analysis to follow.

4. Set-up microprocessor keyboard:

   a. X-Ray Path: only "vac" depressed.

   b. Sample Spin: depressed.

   c. Parameter: all buttons up.

   d. Priority: only "element" depressed.

   e. Scanning Mode: only "quantity" depressed.

   f. Program Mode: only "group" depressed.

5. Calibrate scintillation counter using Fe (for proportional counter use Si; see 10 below). Key in the following sequence on the microprocessor ten-key pad: stop, clear, 0500, start.

6. Fe (or Si; see 10 below) should be displayed under element on the lighted display. Observe Scaler Timer on right panel of instrument; when counting begins press stop on the ten-key pad. If stop is pressed before counting begins, repeat 5 above. If stop is not pressed in 10 seconds, sample will rotate and repeat set-up and counting. Simply press stop when counting resumes. Do not press stop when goniometer is changing angle or when sample changer is moving (listen for sound of motors operating).

7. All of the knobs referred to below are on the right panel of the instrument. Verify and adjust settings as follows:

   RATEMETER MODULE
   a. Range: white line on 1, red line on x4 (Fe) or x2 (Si).
   b. Time Constant: white line on 0.5.

   PHA SETTER MODULE
   a. White line on Manual Ext.

   PULSE HEIGHT ANALYZER MODULE
   a. Coarse Gain: 6 (this is never changed).
   b. Baseline: turn to 170.
   c. Window: 200 (this is never changed).
   d. Mode: turn to "Diff x 0.1".

8. Pull out chart recorder, remove cap from pen and place in holder, depress power and chart buttons on left side of chart recorder, pen should move. If necessary, change RATEMETER range setting so pen reads between 50-70 on chart paper. Obtain average reading with baseline at 170, turn baseline to 230 and compare averages. If averages are different (generally the case), open the right panel door above the microprocessor and use screwdriver (located by sample chamber door) to adjust the SC (PC for Si) adjustment screw, so that the average for either the 170 or 230 reading is half-way between the 170 and 230 averages. Check both readings and continue to adjust until the two readings are very close, within one division on chart paper (each division is about 2.3 mm). This insures that peak will be at 200. When done, turn off the power and chart recorder buttons. Set baseline to 060 and mode to "EXT 2" on PULSE HEIGHT ANALYZER MODULE. Replace cap on pen.

9. Record the counts on the Fe or Si peaks.

   On SCALER TIMER MODULE check and set:
   a. Preset: white line on 10, red line on 1 (10 seconds).
   b. Depress black rectangular start button.
   c. Record scaler value on sheet next to telephone. If scaler value is not within 1000 counts of previous

reading, check module settings and repeat calibration if needed.

10. After calibration for Fe is complete, calibrate proportional counter using Si peak (major elements only). Enter the following sequence on the microprocessor ten-key pad:

    stop, clear, 0600, start

    Repeat steps 6 through 9, adjusting PC instead of SC and using settings given for Si.

11. Check that cap is on recorder pen, push in chart recorder, remove calibration standard and insert the appropriate intensity reference (PART C) in position 1. If you haven't already done so, insert samples into the chamber and make the appropriate entries in the log book. Make sure all samples advance before closing sample chamber door (see PART C above).

PART E Computer Setup, Trace & Major Element Analyses

COMPUTER POWER-UP:

Depress ON LINE button on microprocessor panel. Turn computer and printer terminal on. (Computer on/off switch is large, clear rectangular button located on upper right panel of RT-11. Printer terminal on/off switch is white button located below Decwriter keyboard on lower left.) Printer should verify by typing "Starting system". Wait about 30 seconds for computer to boot from hard disk. When printer returns a period prompt (.), you can begin your analysis. If a message is printed out which ends with the statement "Press the RETURN key when ready to continue", you have attempted to boot the system from the floppy drives, which are not required. Locate the four black buttons on the upper right panel of the RT-11. The LOWER left button should be out (i.e. lit by green light), if not, release to this position by depressing and reboot by pressing the LOWER right button. NEVER DEPRESS THE UPPER BLACK BUTTONS ON THIS PANEL. To escape from any of the programs below, press the control and C keys (Ctrl-C) simultaneously and wait for period prompt.

TRACE ELEMENTS

The following elements can be determined: Cr, Co, Ni, Cu, Zn, Se, Rb, Sr, Y, Zr, Nb, Ba, Hf. Running times are for 6 samples. Comments and sample identification can be typed in with Decwriter keyboard by taking the computer off line (depress ON LINE button on microprocessor to up position), return to ON LINE when finished. A return/enter must follow every entry.

1. Co, Ni, Cu, Zn: These elements are determined as a group. Running time about 1 hour, 17 minutes. To implement this program, type XZNCO at the period prompt. Enter the number of samples in the sample chamber (1-6). Before beginning the analysis, be sure to check vacuum gauge (needle in green field), kV (50), mA (45), baseline (060), mode (EXT 2), sample spin (down), and on line button (down). Refer to Part D for locations, readjust if necessary. On the x-ray machine microprocessor keyboard, press: stop, clear, start (to the right of the sample chamber) to begin the analyses.

2. Rb, Sr, Y, Zr, Nb: These elements are determined as a group. Running time about 1 hour, 36 minutes. To implement this program, type XRBNB after the period prompt is returned. Proceed as indicated in 1.

3. Rb, Sr: These elements are determined by typing XRBSR after the period prompt. Running time about 42 minutes. Proceed as indicated in 1.

4. Se: This element is determined by typing XSE after the prompt. Running time about 30 minutes. Proceed as indicated in 1.

5. Ba: This element is determined by typing XBA after the prompt. Running time about 19 minutes. Proceed as indicated in 1.

6. Hf: This element is determined by typing XHF after the prompt. Running time about 30 minutes. Proceed as indicated in 1.

7. Cr: This element is determined by typing XCR (for samples with greater than 150 ppm Cr) after the prompt. Running

time is about 19 minutes. Proceed as indicated in 1. For samples with less than 150 ppm Cr, you must type XRAY after the prompt. Proceed as indicated in 1; but in addition, the numbers of the parameter file and output file are 11 and 48, respectively. Scaler counts will be printed out and concentrations must be manually calculated. Divide background counts by 40 and peak by 100 to normalize to counts/second. The two background counts/second are averaged and subtracted from the peak counts/second. This value is then normalized against the standard (i.e. standard = 1) and ppm Cr is read from the calibration curve, which is kept in the Cr file stored in the left set (nearest the windows) of sliding-glass cupboards. (NOTE: Method used initially for Cr is chosen at the discretion of the analyst depending on rock type and what is generally expected for that rock type. If the first run is not in the correct range, it is run again using the other method.)

MAJOR ELEMENTS

The following oxides are determined: P_2O_5, SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, MnO, Na_2O, K_2O. To enter the major element program, type ESCP at the period prompt. A return (enter) is required after every entry. Running time is about 2.5 hours for 6 samples. The following series of questions will be asked (reply with answers in bold type):

DECSCOPE IN USE (Y/N) ? **N**

DATAFLEX INITIALIZED (Y/N) ? **N**

OPERATING CONDITIONS? (ENTER KV, MA VALUES): **50,45**

COMMENT (TWO LINES USABLE): Enter your comments here. If you only use one line, hit return twice.

Key in "stop", "clear", and "start" on microprocessor key pad to start Dataflex and wait for INITIALIZATION RESPONSE, followed by the ESCP prompt.

ENTER ESCP COMMAND: **P1**

The printer will echo the operating conditions and your comments.

ENTER AOAP COMMAND NO ? **C2**

ENTER SAMPLE POSITION NO'S (START,STOP): **1,6** (1,5 for 5 samples; 1,4 for 4 samples; etc. If less than 6 samples, return may have to be depressed again - See Note 1).

DO YOU WANT TO AVERAGE THESE SAMPLES (Y/N) ? **N**.

ENTER I.D. FOR SAMPLE (1): **BCR-1**

ENTER I.D. FOR SAMPLE (2): **Your sample ID**

ENTER I.D. FOR SAMPLE (3): **Your sample ID**

ENTER I.D. FOR SAMPLE (4): **Your sample ID**

ENTER I.D. FOR SAMPLE (5): **Your sample ID**

ENTER I.D. FOR SAMPLE (6): **Your sample ID**

STANDARD SAMPLE POSITION NO: **1**

ENTER TABLE I.D. (MAX: 8 CHARACTERS!): **JOHNS-**** (See Note 2).

ENTER AOAP COMMAND NO ? **C3**

PRIORITY (SAM/ELM): **ELM**

INTENSITIES (Y/N): **Y**

Note: The next step will start the analysis. Before continuing, be sure to check vacuum gauge (green), kV (50), mA (45), baseline (060), mode (EXT 2), P-10 SCFH gauge at 0.10, sample spin (down), and on line button (down). Refer to PART D for locations; readjust if necessary.

ENTRIES CORRECT (Y/N): **Y** (If you have made mistakes, enter N and the program will recycle).

PART F Shut Down

1. Remove printed results from printer terminal.

2. Turn off printer terminal and computer.

3. Turn P-10 gas to 0 on rectangular gauge.

4. Slowly (15 seconds at each setting) turn down kV and mA settings on the tube voltage and current panel. Be sure to keep the kV value greater than the mA value at all times. Final settings: kV = 20, mA = 2.

5. Remove samples from chamber, close door, turn handle to activate vacuum. Always leave the instrument under vacuum. Remove samples from holders (dust off holders if you had pressed pellet samples) and return holders to desiccator. Turn off sample-advance toggle switch below sample chamber door. Depress sample spin and on line buttons to up position.

6. Replace yellow covers on printer terminal and microprocessor board.

7. Close door.

Note 1: If anywhere in the program, the computer repeats or recycles what has already been entered, simply press return a second time.

Note 2: If only one element is desired, enter: "JOHNS-n" where n is a one or two letter code for the element desired (e.g., Ca, Na, K, P, etc.). To determine several elements (but not all those in the tables), this is repeated individually for each element.

PROCEDURES FOR DETERMINATION OF WATER CONTENT (AS LOSS ON IGNITION)

by

John W. Husler
Department of Geology
University of New Mexico
Albuquerque, NM 87131

First Edition: May 1988

Latest Revision: December 29, 1989

I. Determination of $H_2O(-)$ (Hygroscopic or Non-essential Water.)

Weigh 0.5 to 0.6 ±0.0001 g powdered -100 mesh sample into an ignited (1000±70° for about 15 minutes), cooled (in a desiccator at least 1 hour), and weighed (to ±0.0001 g) platinum crucible. The weight of the above sample (determined by difference from the crucible weight) is referred to in subsequent calculations as "LOI sample weight".

Heat powder in crucible for one hour ±5 minutes at 110±10°C. Cool at least one hour in a desiccator and reweigh. Retain sample for weight loss on ignition (LOI) determination. Calculate $H_2O(-)$ as follows:

$$\% \, H_2O(-) = \frac{B - C}{A} \times 100$$

where A = LOI sample weight
B = Wt. of Crucible + sample before heating
C = Wt. of Crucible + sample after 110°

II. Determination of LOI

Ignite the sample (in crucible) used for determination of $H_2O(-)$ for one hour (±5 minutes) in a box furnace at 1000±70°. Cool in a desiccator for at least one hour and reweigh. (As above, all weighings are made to ±0.0001 g.) LOI is calculated as follows:

$$\% \, LOI = \frac{C - D}{A} \times 100$$

where A = LOI sample weight
C = Wt. of Crucible + sample after 110°
D = Wt. of Crucible + sample after 1000°

III. Determination of $H_2O(+)$

$H_2O(+)$, or combined water, is estimated by **adding** to the LOI a weight equal to the amount of oxygen gained by the conversion of FeO to Fe_2O_3 upon ignition at 1000°. The ferrous iron (FeO) remaining in the sample, if any, is determined in the same manner as for the original (unignited) sample (See "Determination of

Ferrous Iron in Silicate Rocks", TP-61, Appendix F). The following ferrous iron oxidation correction is used to estimate $H_2O(+)$:

$$\% H_2O(+) = \% \text{ LOI (from Part II above)} + \{ H - (E - G) \}$$

where E = Wt. % FeO determined for original sample
F = Wt. % conversion factor Fe_2O_3/FeO = 1.1113
G = Wt. % FeO after 1000°
H = (E-G) X F

After substitution and factoring, this equation reduces to:

$$\% H_2O(+) = \% \text{ LOI} + 0.1113 \times (E - G)$$

Note: Other volatiles in the rock, including CO_2 and organic matter, will be included in the LOI and reported as $H_2O(+)$.

References:

Hillebrand, W.F., and Lundell, G.E.F., Applied Inorganic Analysis, pp. 689-690, John Wiley and Sons, Inc., New York (1929)

DETERMINATION OF FERROUS IRON IN SILICATE ROCKS

by

John Husler
University of New Mexico
Department of Geology
Albuquerque, New Mexico 87131

Last Revised: December 29, 1989

I. INTRODUCTION

The sample is dissolved with hydrofluoric and sulfuric acids, with special care to prevent oxidation of ferrous iron. The ferrous iron is then titrated with standard potassium dichromate using sodium diphenylamine sulfonate as an indicator. The procedures detailed below are modified from procedures outlined by Kolthoff and Sandell (1961) and Furman (1962).

The presence of sulfides, V^{3+}, and organic matter (the latter more so when potassium permanganate rather than dichromate is used for the titration) can lead to high results for ferrous iron due to reduction of ferrous iron. This technique will not yield accurate results for samples which are very rich in organic matter or sulfides. It works fine for most most rock samples which are low in these materials. The presence of elemental iron from pulverizers may also lead to high results; this is reduced by minimizing the use of iron-bearing pulverizing equipment in the crushing procedures.

II. PROCEDURES

A. Preparation of Potassium Dichromate Solution

1. Crush a sufficient quantity (at least 2 grams) reagent grade Potassium Dichromate (K_2CrO_7) in an agate Mortar, then dry for one hour in oven (at 110±10 °C) to remove any adsorbed water, and cool to room temperature in a desiccator.

2. Weigh out 1.3650±0.0001 g K_2CrO_7, and add to 1.00±0.003 L of deionized H_2O in a volumetric flask at ambient temperature. If ambient temperature is greater than 20°C (measured by mercury thermometer above the deionized H_2O container), a correction is made by adding an appropriate amount of H_2O based on the temperature dependence of the density of H_2O. Consult the Table "Temperature Correction for Volumetric Solutions" (Hodgman, 1960, p. 2137) and add the quantity of water (indicated as a negative number in the table) to the solution. (NOTE: Temperature need only be to ±1°C since the error resulting from variations in water density is much smaller than titration error. Ambient temperature in the lab is almost never less than 20°C, and if it is, this solution is not made.) The prepared solution is stored in a

tightly capped glass container, labeled with the composition, concentration, and date of preparation. K_2CrO_7 solution is stable for at least a year.

B. Sample Dissolution

1. Weigh (into a 30 mL clean and weighed platinum crucible) 0.45 to 0.55 g of -100 mesh rock powder to an accuracy of ±0.0001 g and note the weight (by difference) in lab notebook. A 50 mL FTE Teflon (R) beaker can be substituted, in which case the sample is weighed on weighing paper and transferred to the beaker with a minimum amount of deionized H_2O.

2. Add 1-2 mL of deionized water and rotate to moisten the powder.

3. Pour approximately 10 mL of 1:1 sulfuric acid (H_2SO_4) into the crucible (or beaker), cover, and warm on a hot plate under a fume hood.

NOTE: Heating is best done with two hot plates with cleaned surfaces. One is set at a warm temperature (Corning PC 100 setting of 1 or 2), and the other is pre-heated to a hot setting (3 or 4). After HF is added, the sample is immediately transferred to the hot hotplate to commence boiling. This allows for rapid heating without the danger of having the sample spew over upon addition of HF.

4. Move the cover of the crucible (or beaker) slightly to one side with teflon-coated tongs, and carefully pour in approximately 5 mL of 48% hydrofluoric acid (HF). Replace the cover and heat to boiling without delay. Boil gently for about ten minutes; boiling must be uninterrupted, and care should be taken to protect from drafts.

5. While sample is being decomposed, fill a 400 mL glass beaker half-full of room temperature deionized water and add 15 mL of 1:2 sulfuric acid, 5 mL of 85% phosphoric acid, 25 mL of saturated boric acid solution, and 6 drops of 0.2% aqueous sodium diphenylamine sulfonate. Water must be sufficient for complete immersion of the crucible, and amounts of acid solutions need only be accurate to about ±10%. When

dissolving sample in a Teflon beaker, add only about 150 mL H_2O to the 400 mL beaker to allow for rinsing.

NOTE: Errors can be introduced by oxidation of ferrous iron to ferric in decomposition by HF. Fluorides form very slightly ionized complex ferric fluorides, and therefore in the presence of excess fluoride the oxidation potential of the ferrous-ferric system is lowered to such an extend that air oxidation becomes easy. These errors are minimized by keeping the sample covered (away from drafts) while boiling, and proceeding immediately to the titration.

C. Ferrous Iron Determination

1. Using the tongs, remove the lid, being careful not to spill any solution, swish it gently in the solution, and remove. Using teflon-coated tongs, quickly place the covered crucible in the bottom of the 400 mL beaker, immersing it in the solution. Rinse tongs into the beaker with deionized water. If using a Teflon beaker, pour the contents into the 400 mL beaker (using tongs), rinsing the Teflon beaker and tongs into the 400 mL beaker with room temperature deionized water.

2. Titration is done using a 50mL Class A Buret. Stir and titrate at once with the 1.365 g/L standard potassium dichromate solution. Prior to the titration, note the amount of solution in the buret, estimated to 0.01mL, measured at the bottom of the meniscus, and enter the reading in the laboratory logbook. Initially titrate slowly (dropwise). If no ferrous iron is present, solution will become yellow but will never show any purple color; if a trace of ferrous iron is present, an initial color with one or two drops will be light purple but will not darken with subsequent titration. In either case, the amount of FeO present is recorded as <0.01%. If subsequent drops cause the purple color to appear, continue the titration a few drops at a time, pausing to observe the purple color for permanence. Titrate to the first permanent dark purple (retains color after about 30 sec). When the purple appears permanent, gently swirl the solution in the crucible (in beaker) with a clean glass rod to assure that all solutions are mixed. If color changes, titrate again dropwise until solu-

tion is permanently dark purple. Record the final reading in the buret (as above) and the difference between the initial and final readings in the logbook.

3. After the titration, examine the bottom of the beaker for any dark particles, which would be indicative of incomplete decomposition of the rock. If such are found, repeat the determination using a more finely ground sample. Pyrite, chromite, and garnet are only slightly attacked by hydrofluoric acid, and must be very finely powdered.

4. One mL of 1.365 g/L potassium dichromate will titrate 0.002 g of FeO. Weight percent of FeO is calculated by ratio of the determined weight of FeO to the weight of the sample.

III. REFERENCES

Hodgman, C.D. (Editor), The Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland, Ohio (1960)

Kolthoff, I.M., and Sandell, Textbook of Quantitative Inorganic Analysis, 3rd Edition, The Macmillan Company, New York (1961).

Furman, N.H., Standard Methods of Chemical Analysis, 6th Edition, D. Van Nostrand Co., Princeton, N.J. (1962).

GRAVIMETRIC DETERMINATION OF SILICA IN SILICATE ROCKS

by

John W. Husler
University of New Mexico
Department of Geology
Albuquerque, New Mexico 87131

First Edition: October, 1978
Latest Revision: December 29, 1989

IINTRODUCTION

The sample is fused with sodium carbonate, leached with HCl, dehydrated, and the silica filtered, ignited, and weighed. For the most accurate work, a double precipitation is performed and the silica is determined by weight loss upon volatilization with hydrofluoric acid. Procedures detailed here are based on those described by Kolthoff and Sandell (1961).

II. PROCEDURE

Prepare a representative sample following procedures for preparing powders for whole rock analysis outlined in TP-59 (for SNL YMP work) or in the document SAMPLE PREPARATION IN GEOCHEMICAL ANALYSIS.

NOTE: For all weighings using weighing paper, the paper is handled only with tweezers or with gloves.

Weigh, to the nearest 0.0001 g, a 0.5-0.6 g sample into a clean, dry 30 mL platinum crucible. Weigh out, on tared, glazed weighing paper, pure anhydrous sodium carbonate approximately equal to 5 times the sample weight; e.g., 2.5g Na_2CO_3 per 0.5 g sample. Pour most of the Na_2CO_3 into the crucible and mix intimately with the sample using a platinum wire. Clean the Pt wire by rubbing it in the Na_2CO_3 remaining on the weighing paper, and pour this Na_2CO_3 into the crucible, making a thin, even layer covering the sample.

Cover the crucible with the Pt lid and place on an iron-wire triangle with clay sleeves (clay triangle) over a Meker burner at low temperature. Gradually increase the temperature over the next 10 minutes so that the sample does not spatter on the lid. Next, fuse the sample at the highest temperature of the burner for an additional 10 minutes with occasional swirling of the melt. Finally, remove the lid, and carefully swirl the melt as it cools so as to form a thin layer on the walls of the crucible. If any sample has splattered on the lid, invert the lid over the burner and fuse the melt. This takes about 10 seconds. Set the crucible on a clean clay triangle to cool.

After the sample has cooled somewhat (a minute or two), place the covered crucible in a 250 mL ceramic casserole dish. Slide the crucible lid over enough to add about 5 mL 1:1 HCl (6N), then replace the lid. Cover the whole casserole with a watch glass and let the sample react for 2 to 3 minutes. When the reaction visibly subsides (lid may be removed briefly to check reaction), add an additional 15 mL of 1:1 HCl in small (few mL) increments. When the reaction becomes sluggish, begin scrubbing the crucible and lid with a clean rubber policeman, adding a few additional mL of 1:1 HCl if necessary. At this point, difficult scrubbing can be avoided by allowing the melt to react with the HCl for several hours (or overnight). Keep the casserole and crucible covered with a large watch glass. Quantitatively transfer the sample and washings from the cover and crucible to the casserole dish. When all the sample has been transferred from the crucible to the casserole dish, rinse the crucible and cover thoroughly with 1% HCl (1:50 dilution of 1:1 HCl) and remove them from the casserole. Place the cover and crucible on a clean hotplate and dry. If any sample remains, scrub with 1% HCl and add washings to casserole dish.

Place the casserole on a steam bath or very low temperature hotplate and evaporate until the sample has been visibly dry for at least one hour. (Overnight drying on a hotplate is acceptable, but the temperature should not be allowed to exceed that of a steam bath. The evaporation must take place below about 110°C in order to avoid possible solubilization of the SiO_2 by interaction with Mg, which is usually present.)

Cool, then moisten the entire sample with 10 mL 1:1 HCl, and carefully break up the salts with a rubber policeman. Add 45-50 mL deionized H_2O and warm on a hotplate (LOW setting) to dissolve the soluble salts. Carefully filter the sample through 11 cm Whatman No. 541 (or equivalent) filter paper using a clean glass funnel, reserving a corner of the filter paper for swabbing the dish after thorough rinsing. Depending on the accuracy required, proceed by one of the following routes:

A. SHORT METHOD: Carefully rinse the dish 6-8 times by scrubbing with the rubber policeman, passing all solution through the filter paper. Use small amounts of 1% HCl each time and then swab the dish with the piece of filter paper and add it to the SiO_2 precipitate in the funnel. Rinse the funnel an additional 6-8 times with 1% HCl, allowing the funnel to drain each time. Place the precipitate (with filter paper) in a clean, ignited (1000±70°C for 1 hour), cooled, and weighed platinum crucible. Cover, and dry the paper on a clean low temperature hotplate. Turn the hotplate to high and char the paper (in fume hood). Transfer crucible to a box furnace, and ignite at 1000±70°C for 1 to 1.5 hours, beginning below about 500°C. Cool in a desiccator and weigh the crucible (with precipitate); weight of SiO_2 is calculated by difference.

B. LONG METHOD: Proceed as in A., but retain the filtrate in another 250 mL casserole. Evaporate the filtrate as before, add approximately 5 mL 1:1 HCl, 30 mL H_2O, warm and filter through a <u>second</u> 541 paper. After thorough rinsing (4-6x), place both papers in an ignited, cooled, weighed Pt crucible; ash, cool, and weigh as directed in A.

In a fume hood, moisten the SiO_2 precipitate (which is contaminated with small amounts of Al, Fe, Ti, etc.) with 1-2 mL H_2O, add 2-3 drops 1:1 H_2SO_4 and 10 mL 48% HF. Evaporate to dryness (in a hood), raising the temperature to drive off the H_2SO_4. Start with the hotplate on a setting of 3, and raise to "High" when white sulfuric acid fumes can be seen rising from the mixture. When fumes can no longer be seen, place in a box furnace at 1000±70°C for 30 minutes to one hour. Cool and weigh the crucible again as directed in A. Silica is calculated from the difference between first and second weighings as follows:

$$SiO_2(wt.\%) = \frac{(\text{Wt. of crucible and precipitate}) - (\text{Wt. of crucible \& residual after HF})}{\text{Wt. of Sample}} \times 100$$

III. NOTES

1. The platinum ware can be cleaned by heating with 1:1 HCl or 1:1 HNO_3 or HF + H_2SO_4, but not with HCl + HNO_3. Rinse with water, scrub in soapy water using Scotch Brite (R); rinse with hot tap water followed by deionized water.

IV. REFERENCE

Kolthoff, I.M., and Sandell, E.B., Textbook of Quantitative Inorganic Analysis, 3rd Edition, The Macmillan Company, New York (1961).

PROCEDURES FOR SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHOROUS (P_2O_5)

by

John W. Husler and James R. Connolly
University of New Mexico
Department of Geology
Albuquerque, New Mexico 87131

First Edition: January, 1989

Last Revised: December 29, 1989

INTRODUCTION

Phosphorus (as P_2O_5) is determined colorimetrically by an adaptation of the Molybdenum Blue method (Chen et al, 1956). A colorimetric spectrophotometer is set to read concentration directly based on the concentration in a known rock standard, and the data are recorded in a laboratory notebook.

The standard, sample and blank solutions used are those previously prepared for determination of elements with AA. See "Analytical Methods for the Determination of Major Elements in Rocks Using Atomic Absorption Spectrophotometry" for methods of preparation.

PRELIMINARY:

1. Check that the meter on the Bausch & Lomb Spectronic(R) 88 spectrophotometer reads exactly 0.0 (needle visibly centered over the zero mark) with power OFF. (Refer to "Meter Zero Adjust" in spectrophotometer operating manual if adjustment is required.)

2. Turn power ON with rear panel power switch, and allow instrument to warm up a minimum of five minutes.

3. Fill two 1 liter beakers half full of deionized water, and place on hotplate to boil.

PREPARING PHOSPHORUS REAGENT:

The reagent as prepared below is sufficient to analyze 24 samples and standards. The prepared reagent must be used for P_2O_5 determinations within an hour of completing step 3 below.

1. Solution A: Dissolve 3.20±0.01 g of ammonium molybdate (tetra hydrate) in 40±1 mL deionized H_2O.

2. Solution B: Dissolve 4.0±0.01 g ascorbic acid and 1.2±0.01 g sodium fluoride in 40±1 mL deionized H_2O.

3. Add Solution A to 200±1 mL of 5% H_2SO_4. Mix well. Follow with Solution B. Mix. 10 mL of this reagent is used for each 3 mL of sample (see below). The solution should be slightly yellow colored.

PHOSPHOROUS DETERMINATION

1. Pipet 3 mL each of the undiluted blank, standard (0.1 and 0.2 g), and sample solutions used for the AA determination of Al, etc., into 30 mL test tubes. Pipet 10 mL of Phosphorus reagent into each test tube. Make sure the bottom of the meniscus is in the same position for each solution, and use a bulb to deliver the reagent, exerting enough pressure to cause the reagent to mix well with the 3 mL of sample. This will, of course, not deliver exactly 10 mL using a volumetric pipet in this manner, but since all samples and standards are treated similarly, the pipeting error will be negligible. Error in precision between solutions is estimated to be that of 10 mL Class A pipets, or ±0.02 mL.

2. Place the test tubes in a boiling water bath (half-full, one liter beakers). Remove the beakers from the hotplate to avoid bumping, and allow the test tubes to remain in the beakers for 7±0.5 minutes. Cool the tubes to room temperature by placing them in a beaker of cool tap water for a few minutes. Repeat with a second beaker of cool tap water, then transfer solutions to one cm colorimetric cells.

3. Set mode selector switch on the spectrophotometer to "Absorbance 0-1".

4. Set wavelength by adjusting Wavelength Drive Knob to 820 nM (visual inspection). This is not adjusted again until determinations are complete.

5. Enter in the laboratory logbook the date, time and name of analyst followed by the name of the standard used, the concentration of the solutions (i.e., 0.1 g, 0.2 g, etc.), and the weight percent of P_2O_5 in the standard rock.

6. Insert the blank in the instrument, and zero the meter (visually) by adjusting the "100%T/Zero A" knob. (NOTE: Wipe the exterior of each colorimetric cell with a (Kimwipe or equivalent) laboratory wiper, removing all visible spots from the exterior surfaces, prior to inserting the cell in the instrument.

7. Set mode selector switch to "Concentration".

8. Insert the known 0.2 g standard solution, and set value on meter to the weight percent of P_2O_5 in the rock standard. If the 0.1 g standard solution is used, set the meter to half of that amount. The solution used is selected based on similarity to the samples analyzed, based on what is expected given the chemistry of the samples. If the "high" standard is used and sample values are low, the scale may be reset with the "low" standard, and samples rerun. In the logbook, enter the standard used (i.e., UNM-B1, NBS-SRM-688, etc.), and the amounts read for each standard solution. For the blank and standard used to set the meter, enter an equivalence symbol (i.e., UNM-B1 0.2g ≡ 0.810%) and for the other standard enter the amount read (i.e., UNM-B1 0.2g = 0.405%). With the low P_2O_5 concentrations present in most rocks, the variation from linearity due to the exponential relationship between concentration and absorbance is minimal.

9. Insert sample solutions, read amounts present in the rock samples directly from the meter, and record these in the logbook. If any of the sample absorbances are off scale, the procedure can be repeated using the previously prepared 1:10 dilutions of the samples, reducing the amount read on the scale by a factor of 10.

10. After all samples have been run (up to 18), rerun the standard solutions as a check, and note the values in logbook. Up to 24 samples may be run in the same group. For 18 to 24 samples, run standards after the first half of the samples and again after all samples are completed. The colorimetric spectrophotometer is normally very stable, but if there is a variation of more than ±0.002% between standard runs (with the 0.2g solution of UNM-B1), a drift correction may be made and applied to the standard amounts. This is done by constructing a simple linear drift curve, and adjusting the sample amounts accordingly based on the order in which data were collected. If the variation (with the 0.2g solution of UNM-B1) exceeds ±0.005%, then the initial standard reading is presumed to be in error, and the determinations are repeated including pre- and post-sample standard runs. Include the calculations and corrections in the log book.

Reference Cited:

Chen, P.S., Jr., Toribara, T.Y., and Warner, H., Anal. Chem., 28, 1756-1758 (1956).

SNL NWRT 6310

Interim Change Notice (ICN)

YMP

ICN Number 1 **Page** 1 **of** 1

Document Type And Number TP 61 **Current Revision** A

Title Procedures for Laboratory Sample Bulk Chemical Determination

Description and Rationale for Change:

1) Delete 2nd to the last sentence in the 2nd paragraph of Section 6.2 (page 14) and insert a Section 6.3 (bump current 6.3 to 6.4) titled QA Records which states:

QA records, including corrections and changes thereto, generated as a result of implementing this procedure, shall be prepared and submitted to the SNL NWRT Department Records Center in accordance with QAIPs 17-1 and 17-2 and the "Master List of File Codes" by the responsible SNL PI.

The following is a list of QA records that may be generated by the implementation of this procedure:

1 Whole-Rock Analysis Worksheets (Appendix A)
2 Computer printouts
3 Pages containing calculations of analytical results
4 Strip-charts (if specifically requested in the governing EP)
5 Standard curves (if AA analysis is used)
6 Pages from laboratory notebooks
7 Summary report from chemist to PRS
8 Chain-of-Custody forms for samples
9 Deviation reports, if any

If this procedure is used without a governing EP, all of the above will be submitted as QA records generated by use of this procedure. If a governing EP exists, records in Categories 1 and 7 will become part of an experiment logbook that will be submitted as a QA record generated by use of the EP.

2) Add QAIP 17-1 and 17-2 and the "Master List of File Codes" to the reference list in Section 8, page 16.

Rationale: Necessary to accommodate QAIP 5-2, Rev 00.

(Identify the ICN by number next to the affected procedure paragraph, insert change, if desired, and file ICN with the affected procedure.)

Approvals:

Author [signature] Date 2/6/91

Division Supervisor [signature] Date 2/6/91

QA Division Supervisor [signature] Date 2/8/91

Department Manager Thomas E. [signature] Date 2/9/91

Effective Date 3/1/91

NWF 5-1.2/1-2(1/22/91)

SNL NWRT 6310

Interim Change Notice (ICN)

YMP

ICN Number 2

Document Type And Number ~~TP 61~~ Current Revision ~~A~~

Title ~~Procedures for Laboratory Sample Bulk Chemical Determination~~

Description and Rationale for Change:

This change affects procedure wording specified in ICN #1 to this TP.

Change, in the "Records" section of the TP, as established by ICN #1, wording that states, " The following is a list of QA records that may be generated by the implementation of this procedure.", to read, " The following records, if generated by the use of this TP, shall be submitted as QA records."

Rationale: This change clarifies that initiation of the subject documents and treatment of them as QA records, is not optional.

(Identify the ICN by number next to the affected procedure paragraph, insert change, if desired, and file ICN with the affected procedure.)

Approvals:

Author [signature] Date 3/28/91

Division Supervisor Francis Mimick Date 4/3/91

QA Division Supervisor [signature] Date 4-3-91

Department Manager Thomas E Blejwas Date 4/4/91

Effective Date 4/14/91

SNL NWRT 6310

Interim Change Notice (ICN)
(Continuation)

YMP

ICN Number 2

Page 2 of 2

Document Type and Number TP 61

Current Revision A

Title Procedures for Laboratory Sample Bulk Chemical Determination

Description and Rationale for Change:

Additional Signature Lines

Date 4/3/91

Principal Investigator

Date 4/3/91

Independent Technical Review